# PREFACE

THIS book is intended primarily for students of the Massachusetts Institute of Technology, and represents the work planned for those who have finished the excellent introductory course in "Quantitative Analysis" by Professor Henry P. Talbot. Assumption has been made that the student is familiar with the use of the balance, the principles of volumetric analysis, and of stoichiometry, and no attempt has been made to enlarge upon these subjects. The material offered is chosen to illustrate principles and to train the student in manipulation. In certain cases a student is offered a choice of method, as in the determination of sulphur in pyrite, and in other cases where the principle differs, as in the determination of manganese in steel, it is desirable that the student acquaint himself with each method.

The student is earnestly requested to read and understand each method before beginning any laboratory work. Adequate preparation of apparatus should also be made.

In preparing this volume the author wishes to express his appreciation of the helpful suggestions of Professor R. S. Williams, and of the kindly services of Mr. L. F. Hamilton.

HENRY FAY.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
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SAMPLING FOR ANALYSIS

THE selection and preparation of a sample for analysis, whether it be an ore, rock, mineral, or metal, is just as important as the method of analysis itself. In a brief discussion of the subject it is very difficult to lay down general rules for making the samples owing to the varying conditions, such as size of shipment, or the character of the ore or metal. The desired end is to obtain a sample which will be representative of a whole shipment, whether it be a car load, a train load, a cargo, or a large or small shipment of metals in their varied forms. Many of the controversies between producer and consumer may be traced to inequality of sample. The sampling by the producer and consumer in the case of ores is done usually under very different conditions and it is quite remarkable that there should be such close agreement rather than that there should be much divergence.

Inasmuch as the principle of mineral or rock sampling is in general the same, the sampling of a car of ore will be taken as typical. Immediately on receipt of the car, samples should be taken by means of a small shovel or trowel from various parts of the car. The best method of getting even distribution is to take a one- or two-pound sample from a large number of places, the car being divided so as to obtain the samples at equal distances from the centre and ends, as well as between; or the car may be sampled along a zig-zag line running from one corner to the diagonally opposite corner, crossing the car at one-third and two-thirds of the length. This method must be followed not only at the surface of the car, but also midway between top and bottom and near the

bottom of the car. When lumps are encountered, small portions of each lump must be chipped off and an equal portion of fine must be taken adjacent to the lump.

The total sample is then mixed, piled in a cone and alternate quarters rejected. The material thus obtained is further subdivided by crushing or grinding, and again coned and quartered, and this process continued until a one- or two-pound sample which will pass through a 100-mesh sieve is obtained. In rock or mineral sampling, it is absolutely necessary to crush or grind all of the quarters taken and not to reject any portion on account of extreme hardness or softness. This would defeat the end which is aimed at.

Precaution should also be taken when removing a sample from the general supply bottle as there is strong tendency for the coarser particles to find their way to the bottom of the container. The bottle should be well shaken, or preferably rotated on a wheel, or the contents spread out and mixed on a large piece of glazed paper. Unexpected variations may arise from year to year from neglect of this precaution.

The sampling of ores is made difficult by the uneven character of coarse and fine, hard and soft, material, and of minerals of high and low specific gravity. The degree of fineness to which a mineral or ore is ground is also an important factor. Many analyses are affected due to failure to take this fact into consideration. In the determination of water, sulphur in pyrite, or ferrous iron in silicates large variations may occur between different analysts because of the differences in the fineness of the samples used. In fine grinding oxidation of sulphur or iron may occur, or there may be loss of water. It is advisable in such cases to make determinations on both fine and coarse material.

The difficulty of sampling metals is principally due to the tendency to segregation in the ingot, or cast form. This tendency is due to the fact that during solidification selective crystallization takes place and thus produces a melt richer in one or more constituents which solidify at a lower temperature. When a metal passes from the liquid to the

solid state, the outside skin solidifies first on account of the more rapid conduction of heat from the surface, and thus leaves a molten interior. This molten mass gives up crystals to those already formed and there is a constant enriching of the material in the melt. In steel, carbide and phosphide of iron are thus concentrated and are always segregated in that portion of an ingot last to solidify, *viz.:* in the upper central portion of the ingot.

Again, compounds of lower or higher specific gravity than the main mass of the melt may form and thus rise or fall in the still molten mass. A good example of this type of segregation is in the case of sulphur in steel which is always combined with manganese as manganese sulphide and being of lower specific gravity than the steel itself rises to the surface of the melt.

Due regard to segregation must be made in the sampling of any cast metal. In products which are forged from the ingot the segregation persists in the forged material irrespective of shape. Rigid specifications for steel usually call for the rejection of definite portions of the top (usually 25 per cent) and bottom (usually 5 per cent) of the ingot, but even in spite of these precautions, differences are invariably found. It is never safe to assume that any metal is uniform and it is much better to assume that it lacks uniformity and proceed accordingly.

In the sampling of a steel rail, for instance, it would be foolish to assume that a single sample would represent the whole unless that single sample were obtained by boring a hole entirely through the rail from top to bottom. Even so this method would not be so satisfactory as taking samples from a number of holes distributed over the head, foot, and web, or better by planing over the whole surface. In all cases, as much of the surface as possible should be represented in the sample.

If possible, a macroscopic survey should be made before sampling any steel if the material is likely to be a subject of controversy. To this end, a cross section of the piece is fairly smoothly polished and then etched either with an 8 per cent

solution of copper ammonium chloride [1] or a 6 per cent solution of iodine in alcohol. In the former case segregated carbide and phosphide appear darker than the surrounding metal, and in the latter case phosphide in particular appears lighter colored. Interpretation of results thus obtained should always be left to those experienced in this work.

It is needless to add that the tool with which metal samples are taken should be free from oil.

DETERMINATION OF SILICA IN A DECOMPOSABLE SILICATE

LAUMONTITE

Weigh approximately 0.5 gram of the finely ground material into a 300 cc. porcelain casserole. Add about 25 cc. of water, and stir until the silicate is completely wet. Now add in small portions 25 cc. hydrochloric acid (sp. gr. 1.12), heating the casserole and stirring the contents during the addition of the acid, and continuing the heating until the silicate is completely decomposed or until no gritty residue is left. Evaporate the solution to dryness, stirring frequently if there is any tendency toward the formation of a jelly-like mass. When completely dry, add just enough concentrated hydrochloric acid to moisten the residue, and evaporate again. Moisten the residue again with concentrated hydrochloric acid, warm gently, then dilute with 200 cc. of water, and heat to boiling. Filter off the silica as soon as it settles, without attempting to remove that which adheres to the wall of the casserole, and wash with hot dilute hydrochloric acid (one part acid, sp. gr. 1.12, to three parts water) until the filter paper is free from iron stain. Finish the washing with hot water, and wash until free from chlorides.

Evaporate the filtrate and washings to dryness in the same casserole, and treat exactly as in the first evaporation, receiving the recovered silica on a second filter paper, and removing the silica adhering to the walls of the casserole by means of

[1] Heyn. International Soc. for Testing Materials, Brussels Congress, 1906.

a rubber "policeman." Wash as before, and then transfer the partially dried filter papers to a platinum crucible. Place the crucible on its side and, by means of a low flame placed under the front of the crucible, smoke off the paper at a low heat. When the volatile products are removed, place the full oxidizing flame of the Tirrill burner at the rear of the crucible, and heat until the residue is white. Finish the ignition, with the crucible covered, over a Meker burner or blast lamp, and heat to constant weight.

When constant weight has been obtained, add to the crucible one or two drops of water, and then 3 to 4 cc. of hydrofluoric acid. Add one or two drops of dilute sulphuric acid, and heat gently in a hood with good draught, until all of the silica has volatilized. If there is considerable residue it may be necessary to repeat the treatment with hydrofluoric acid. When all of the silica has volatilized, heat over the Tirrill burner, and finally over a Meker burner or blast lamp for a few minutes. The loss in weight represents the amount of SiO_2 present.

DETERMINATION OF SILICA IN A REFRACTORY SILICATE

FELDSPAR

Mix thoroughly in a platinum crucible approximately 0.50 gram of finely ground feldspar with about six times its weight of pure, dry sodium carbonate. Place the covered crucible over a small flame and gradually raise the flame to full heat and continue heating for 20–30 minutes, or until effervescence has ceased. Now place the crucible in the oxidizing flame of a Meker burner or blast lamp, directing the flame at an angle, if the blast lamp is used, against the side and bottom of the crucible, and continue heating for five minutes. At the end of this time shut off the gas supply suddenly and allow the air blast to play upon the covered crucible until cool. Place the crucible top side down in a porcelain casserole and gently tap until the solidified mass is removed. If the Meker burner is

used the best method of removing the melt is to insert into the molten mass the coiled end of a platinum wire and allow the mass to solidify around the wire. When cool, reheat gently with a small flame so as to soften the edges and at the same time put the wire under tension. If properly done this should remove the melt as a whole. Wash with hot water the material adhering to the cover and crucible into the casserole and then proceed with the decomposition and determination of the silica exactly as described in the preceding method.

Notes. — 1. The ease with which any silicate is decomposed is determined by the ratio of base to acid. In the more basic silicates, hydrochloric acid will decompose them readily. Such silicates are referred to as soluble or decomposable. With increase in the ratio of silica to base the decomposition with acids takes place less readily, and when the silicate is distinctly acidic in character there is little, if any, action by dilute acids. The latter type of silicate is called refractory, or undecomposable. Such silicates may, however, be rendered decomposable by converting them into basic silicates by fusion with sodium carbonate, lead oxide, or other similar basic compounds. In this way the proportion of base to silica is so raised as to make them easily decomposable by dilute acids.

Most of the artificial silicates, such as the various metallurgical slags, Portland cement, etc., are decomposable.

Certain silicates occurring as minerals are insoluble in their natural state, but, when brought to the fusion temperature, are converted, after cooling, without change of composition, into soluble silicates.

2. When strong acid is brought in contact with decomposable silicates silicic acid is separated in gelatinous form which encloses particles of undecomposed silicate. On evaporation this jelly-like mass dries around the unattacked particles and protects them from the action of the acid. In order to avoid this difficulty, the silicate is first moistened with water, and small amounts of acid are added from time to time so as not to have it in excess until after the decomposition has taken place. By the cautious addition of acid the whole of the silicate may be brought into solution and no silica will separate until the solution has been concentrated somewhat.

Stirring and breaking up of the jelly, when once formed, aids the evaporation and also prevents spattering.

3. The recovery of silica by a second evaporation after the filtration of the major portion seems to be absolutely necessary. Formerly it was the custom to recover the silica passing into the filtrate after a single evaporation by evaporating the precipitate of iron and alumina produced by ammonia with either hydrochloric or sulphuric acids, or to correct the ignited oxides of iron and alumina for silica by fusion with potassium pyrosulphate. The double evaporation method, with intervening filtration, seems to be more efficient and less cumbersome.

The necessity of the recovery of the silica passing into the filtrate after a single evaporation was early recognized by Bunsen,[1] later by Ludwig,[2] and by Meineke,[3] and more recently by Cameron,[4] and Hillebrand.[5]

Invariably small amounts are recovered by the second evaporation, and consequently the operation should never be neglected. This process has the distinct advantage over other methods in that no silica is introduced through the use of ammonia, which always carries from small to large amounts.

4. The temperature of drying the siliceous residue has been the subject of considerable investigation and much difference of opinion.

According to the work of Gilbert [6] and of Hillebrand,[7] drying temperatures above that of the steam bath have little advantage and are sometimes the cause of considerable silica going into the filtrate on account of recombination of silica at the higher temperatures. Furthermore, silica so obtained frequently contains large amounts of impurity. Blount [8] recommends a temperature of 200° for the determination of silica in Portland cement, but this is advisable only in certain special cases and should not be adopted for general work.

[1] *Am. Chem. Pharm.*, **61**, 265.

[2] *Z. anal. Chem.*, **9**, 321.

[3] *Repert. anal. Chem.*, **7**, 215.

[4] *Chem. News*, **69**, 171.

[5] *Bulletin 422, U. S. Geol. Survey*, p. 91.

[6] *Tech. Quart.*, **3**, 61.

[7] *J. Am. Chem. Soc.*, **24**, 262.

[8] *J. Soc. Chem. Ind.*, **21**, 1217.

5. The final temperature of ignition for silica, as well as for other oxides, such as Al_2O_3, Fe_2O_3, TiO_2, SnO_2, etc., must be high. It is claimed by many investigators that this heat is necessary to deprive the silica of the last traces of water, although the evidence is not conclusive that moisture alone is the cause of variation in weight. It has been shown by experiments conducted in this laboratory that in many cases sodium or potassium salts are the cause and that it is necessary to have a prolonged high temperature to remove the traces of alkali which had been occluded by the silica.

When igniting to constant weight, it must not be forgotten that some platinum crucibles lose weight steadily, and the rate of loss should therefore be determined for such a crucible.

6. Silica, as determined by evaporation to dryness, is never absolutely pure, but is always contaminated by traces of aluminum, iron, calcium, or magnesium. The weight must always be corrected by volatilizing the silica as fluoride and weighing the residue after heating as before. This residue, although frequently small, should never be neglected.

7. Sodium carbonate is invariably contaminated with silica and other impurities. For analytical purposes it should either be purified by recrystallization, or the amounts of silica, etc., should be carefully determined. One should never be deceived by a label and should prove to his own satisfaction the presence or absence of impurities. If a sample of pure sodium carbonate be prepared or the amount of silica be determined, such a sample should be carefully guarded and used only for silicate analyses.

Sodium bicarbonate has been recommended as a flux and has much to commend its use, but it is very seldom employed.

8. Lead oxide,[1] bismuth oxide,[2] and boric oxide [3] have been proposed for the decomposition of refractory silicates. By the use of these substances there is not only the distinct advantage that all of the flux may be removed — lead and bismuth by means of hydrogen sulphide, and boron by means of methyl alcohol — thus preventing adhesion of sodium salts, but sodium and potassium may be determined in the same

[1] Berthier, *Ann. de Chim. et de Phys.* (2), **17**, 28.

[2] Hempel, *Z. anal. Chem.*, **20**, 496.

[3] Jannasch and Heidenreich, *Z. anorg. Chem.*, **12**, 208.

sample. These methods have much to commend them, but they have not been extensively used. The principal objection to the first two is the easy reducibility of lead and bismuth either by the reducing flame of the burner or by the presence of organic matter. This objection is not valid if ordinary precautions are taken.

Hillebrand has urged two objections against the boric oxide method, *viz.:* the deposition of boric acid due to the hydrolysis of the volatile boric ether, and the use of the oxygen flame when the alkalis are to be determined. Another very important objection is the difficulty in preparing the flux in pure and finely divided condition. Fused boric oxide is almost as difficult to handle as some of the hardest minerals.

9. It is evident that the methods given are not applicable to the determination of silica in minerals which also contain fluorine. For a method consult page 184, *Bulletin* 422, U. S. Geological Survey.

DETERMINATION OF POTASSIUM AND SODIUM IN SILICATES

METHOD OF J. LAWRENCE SMITH

Weigh into a clean, dry, porcelain mortar 0.5–1.0 gram of finely ground feldspar. Weigh an equal quantity of dry ammonium chloride into the mortar. Place the mortar on a piece of glazed paper and stir carefully with the pestle until the feldspar and ammonium chloride are thoroughly mixed. Weigh out eight parts of calcium carbonate, free from alkali, and transfer gradually about three-quarters of this amount to the mortar, mixing it with the feldspar. Transfer the mixture to a platinum crucible, and use the remaining carbonate to clean out the mortar, placing this on top of the main portion, as a cover. Place the lid on the crucible, and heat so gently for fifteen minutes that the ammonium chloride is not visibly volatilized, but that the odor of ammonia is distinctly perceptible. Then heat for forty-five minutes, so that the lower third of the crucible is red. The proper degree of heat can be obtained if the crucible is placed

just over a flame which has been lowered to about three-quarters of an inch in height.

When cool detach the sintered mass from the crucible and place it in a casserole. Pour on it about 150 cc. of hot water and allow it to stand until the mass has softened. Then cautiously crush and grind until no lumps remain. Boil the water for a few minutes, allow the residue to settle, and decant through a filter into a large casserole. Repeat the boiling and decantation, using about 50 cc. of water each time until the wash water is free from chlorides, finally throwing the insoluble residue onto the filter and washing with hot water. As the process of washing free from chlorides is a tedious one, it is advisable not to begin testing until at least 500 cc. of wash water have been used, and then by using very small quantities and comparing with a blank containing the same quantity of reagents.

Add to the filtrate a slight excess of ammonium carbonate solution, a drop or two of ammonia, and then concentrate to about 100 cc.

Filter the calcium carbonate on a small filter paper, and receive the filtrate and washings in a platinum dish. Evaporate the solution to dryness, and then *cautiously* expel the ammonium salts, taking care not to allow the bottom of the dish to become red. When cool dissolve in a small quantity of water, add one or two drops of ammonia, and ammonium oxalate drop by drop until no further precipitation takes place. Digest on a water bath for a quarter of an hour, and again filter through a small filter. Evaporate the filtrate to dryness, and again cautiously ignite to remove ammonium salts.

The residue, which should be nearly white, is ready for weighing after drying in a desiccator. It should consist of the chlorides of sodium and potassium, unless lithium is present.

To separate the sodium and potassium proceed as follows: Dissolve the weighed residue in a small quantity of water. The solution should show no evidence of insoluble matter. Add one or two drops of hydrochloric acid (sp. gr. 1.12) and about one and one-half times the calculated amount of

hydrochlorplatinic acid, assuming the total weight of chlorides to be sodium chloride. Evaporate the solution over a beaker of hot water, taking care not to allow the water to boil. The evaporation should continue until a crystallized crust has formed over the surface and only 1 or 2 cc. of solution are left. When removed from the water bath the whole mass should be dry. Cover the residue with a liberal amount of absolute alcohol, crush the salts with a glass rod, and stir at frequent intervals for a half hour. Decant the liquid through a weighed Gooch crucible, wash thoroughly with alcohol until the washings run through colorless, and a drop evaporated on a piece of clean platinum leaves no residue. Dry to constant weight at 110°.

The precipitate should consist of a heavy yellow powder composed of octahedral crystals, having the composition represented by the formula K_2PtCl_6. It should be entirely free from the orange-colored sodium salt $Na_2PtCl_6,6H_2O$, and from crystals of sodium chloride.

Notes. — 1. The reaction upon which the method is founded may be represented as follows:

$$2KAlSi_3O_8 + 6CaCO_3 + 2NH_4Cl = 6CaSiO_3 +$$
$$6CO_2 + Al_2O_3 + 2KCl + 2NH_3 + H_2O.$$
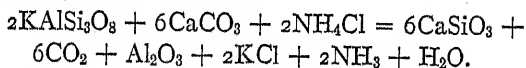
In addition to this reaction there is also, of course, considerable decomposition of the calcium carbonate to calcium oxide and some formation of calcium chloride, both of which appear in the filtrate in the water extract. The completeness of the reaction is dependent upon the fineness of the sample and the care exercised in mixing the sample with ammonium chloride. The heat necessary to complete the reaction is not great, if sufficient care has been taken to have a finely ground sample; but it is preferable, if possible, in order to ensure complete decomposition, to use the long platinum crucible, closed by a cap, as recommended by J. Lawrence Smith.

In case the silicate contains much ferrous iron, the mass, instead of sintering, will fuse to a hard cake. In cases of this kind it is necessary to increase the amount of calcium carbonate.

Silicates may also be decomposed by means of sulphuric

and hydrofluoric acid, but this method has the disadvantage that it is necessary to remove iron, aluminum, magnesium, etc. Each of these substances may carry down more or less sodium and potassium. In the J. Lawrence Smith method these substances are removed in the beginning of the operation, being precipitated by the calcium hydroxide.

In case it is necessary to remove magnesium from a solution in which sodium and potassium are to be determined, it is undesirable to use the phosphate separation on account of the difficulty of the removal of the excess of the reagent. It is much better to convert the magnesium, sodium, and potassium into chlorides, and then to heat with mercuric oxide.

$$HgO + MgCl_2 = MgO + HgCl_2.$$
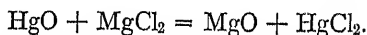
The excess of mercuric oxide and mercuric chloride can be volatilized, and the potassium and sodium chlorides can be separated from magnesium oxide by means of water.

The alkalies may also be determined when the silicate is decomposed by means of lead oxide, boric acid, bismuth oxide, etc.

2. One of the defects of the method is the fact that the calcium carbonate invariably contains small amounts of alkali, principally the sodium salt; but by making a blank determination this may be corrected. The amount of impurity should be placed on the label of the bottle of calcium carbonate, and this sample should be preserved for this determination only. The ammonium chloride may be purified by sublimation.

3. In addition to the removal of the calcium it may also be necessary, in case the rock contained sulphur, to remove small amounts of sulphate. This would cause a contamination of the potassium chlorplatinate on account of the insolubility of sodium sulphate in alcohol. Its removal may be accomplished by the addition of a drop or two of barium chloride, and the removal of the excess of the latter by means of ammonium carbonate.

The removal of the calcium by means of ammonium carbonate has the distinct advantage that the products of its hydrolysis

$$(NH_4)_2CO_3 + 2H_2O \rightleftharpoons 2NH_4OH + H_2O + CO_2,$$
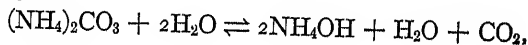
are more or less completely removed in the process of evaporation. With ammonium oxalate, however, there is more or less accumulation of oxalic acid, which upon heating gives considerable carbonaceous material which is difficult to remove from the solution.

4. The separation of potassium from sodium is based on the fact that potassium chlorplatinate is insoluble in alcohol, while the sodium chlorplatinate and excess hydrochlorplatinic acid are soluble. As there is some danger of hydrolysis of the potassium chlorplatinate, according to the reaction,

$$K_2PtCl_6 + H_2O \rightleftharpoons K_2PtCl_5OH + HCl,$$
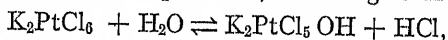
it is necessary to make the separation in the presence of a drop or two of hydrochloric acid to prevent this. After the addition of hydrochlorplatinic acid it is advisable to protect the solution from dust, which would cause a partial reduction to metallic platinum. To confirm the result the potassium chlorplatinate may be reduced by heating with dry oxalic acid, and the metallic platinum may be weighed, or the chlorine in the potassium chloride may be determined. The reaction taking place is shown in the equation,

$$K_2PtCl_6 + (COOH)_2 = 2KCl + Pt + 2HCl + 2CO_2 + Cl_2.$$
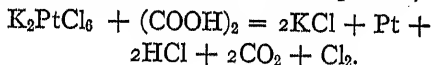
This method may also be applied to the filtrate containing the sodium, finally converting the sodium into sodium sulphate.

5. Instead of weighing the potassium chlorplatinate on a Gooch crucible it may be filtered on paper, washed in the usual way with alcohol, and after the washing is complete it may be dissolved in hot water and the solution allowed to run into a weighed platinum dish. After evaporation to dryness this may be weighed.

In all cases precaution must be taken to protect the solution containing the hydrochlorplatinic acid from ammonia. Otherwise there will be formation of ammonium chlorplatinate.

THE PERCHLORATE METHOD FOR POTASSIUM

After weighing the chlorides of sodium and potassium, obtained as in the preceding process, finish the separation as follows: Dissolve the mixed chlorides in 20 cc. of water, and

add sufficient 20 per cent solution of perchloric acid to convert both sodium and potassium into the perchlorates and to have a slight excess. Evaporate to dryness. Dissolve in 10 cc. of water and add a small amount of perchloric acid. Evaporate again to dryness and repeat this process until dense white fumes of perchloric acid appear. *Allow to cool*, and take up with 25–30 cc. of 97 per cent alcohol, containing 0.20 per cent perchloric acid (1 cc. of 20 per cent solution to 100 cc. of 97 per cent alcohol). Break up the residue with a stirring rod, decant the clear liquid through a Gooch crucible containing an asbestos mat which has been washed with 0.20 per cent perchloric acid in alcohol. Wash several times by decantation with alcoholic perchloric acid solution, transfer the residue to the filter, and wash several times on the filter. Dry the crucible at 120° for one hour, cool, and weigh as $KClO_4$.

Notes. — 1. Potassium perchlorate is insoluble in 97 per cent alcohol containing perchloric acid, and the sodium salt is soluble. This method gives satisfactory results, and has the distinct advantage over the hydrochlorplatinic acid method that it is very much cheaper.

The method has been studied by Wense,[1] Caspari,[2] and Baxter[3] and has generally been accepted as accurate, having been adopted as an official method[4] by the fertilizer chemists of Germany. Scholl[5] has applied the method to the determination of potassium in water analysis.

2. The method is not accurate in the presence of sulphate and ammonium ions. The former can be removed by means of barium chloride and the latter by heating.

3. *The perchloric acid solution containing alcohol should never be evaporated.*

Dangerous explosions may result. There is, however, no danger at the ordinary temperature.

[1] *Z. angew. Chem.*, 4, 691 (1891); 5, 233 (1892).
[2] *Z. angew. Chem.*, 6, 68 (1893).
[3] *J. Am. Chem. Soc.*, 39, 249.
[4] *Fifth Internat. Congr. of Appl. Chem.*, 1, 216 (1903); 4, 940 (1903).
[5] *J. Am. Chem. Soc.*, 36, 2085.

4. The precipitate is much less soluble in alcohol containing a small amount of perchloric acid than in alcohol alone.

ANALYSIS OF SPATHIC IRON ORE

DETERMINATION OF SiO_2, MnO, CaO, AND MgO

Weigh into No. 1 lipped beakers two portions of the ore of approximately 0.5 gram each, and dissolve in 15 cc. hydrochloric acid (sp. gr. 1.12), heating to aid the solution. Filter off the insoluble residue, and wash first with dilute hydrochloric acid and afterward with hot water. Ignite the paper and residue at a low temperature, and weigh approximately within 5 milligrams. Cover with *six* times the weight of sodium carbonate and fuse until action ceases. Add a few cubic centimeters of water to the crucible and warm, then wash the contents of the crucible into the original acid solution. Evaporate to dryness on the steam table, moisten the dried mass with 1 or 2 cc. of hydrochloric acid (sp. gr. 1.20), and again evaporate to dryness. Place in a hot closet and keep at a temperature of 110° C. for one-half hour to dehydrate the silica.

Moisten the residue with 5 cc. of *strong* hydrochloric acid and warm. Then add 50 cc. of water and heat until solution is complete. Filter immediately, wash the silica with dilute hydrochloric acid (one part acid, sp. gr. 1.12, to three parts of water) until the filter shows no traces of iron, and then finally with hot water. Evaporate the filtrate for the recovery of traces of silica, as was done in the silicate analysis. Ignite both filters in a platinum crucible and weigh. Treat the ignited silica with one or two drops of water, enough hydrofluoric acid to dissolve it, and two drops of sulphuric acid (1 : 1). Evaporate to dryness in a hydrofluoric acid burner, ignite, and weigh again. The difference in weight represents the silica. The weight of the residue after the hydrofluoric acid treatment should not be more than 1 or 2 milligrams at the most.

Concentrate the filtrate from the silica, adding bromine

water to oxidize the iron to the ferric state. Evaporate almost to dryness, or until the ferric chloride will completely crystallize when allowed to cool. This operation must be carried on with caution. It is necessary to remove the excess of hydrochloric acid, but if the evaporation is allowed to go too far the iron salts will become baked on the bottom of the vessel, and it will then be necessary to dissolve in acid and re-evaporate. When cold add to the ferric chloride 20 cc. of water; solution should be complete. If any silica has escaped dehydration it will show itself at this point, and it will be necessary to filter it off and repeat the evaporation of the filtrate. Transfer the solution to a small beaker and add, from a burette or dropper, sodium carbonate solution until a precipitate forms which will dissolve only in two or three minutes stirring. This point is indicated by the solution assuming an intense red color, and by the ferric hydroxide going more and more slowly into solution. If an excess of sodium carbonate should have been added, it is necessary to add very dilute hydrochloric acid drop by drop, with constant stirring, until the solution clears again; then to bring the solution back to the proper point with sodium carbonate. Having obtained a solution properly neutralized, add 10 cc. of acetic acid (sp. gr. 1.04).

Meanwhile heat to boiling one liter of distilled water for each determination in actual progress, and weigh out as many portions of 3 grams each of sodium acetate. Transfer the solution of the iron ore, together with the liter of hot water, to a 1500 cc. round-bottom flask, and add one portion of the sodium acetate dissolved in a little hot water. Bring the solution to boiling and continue the boiling for three minutes. If there is any tendency to froth this may be overcome by pricking the bubbles as they form in the neck of the flask with a long, glass stirring rod. Remove the flask from the lamp and allow the precipitate to settle. The supernatant liquid should be colorless and clear.

Filter, while *still hot*, through a 24 cm. fluted paper. Wash once by decantation with 250 cc. of hot water. Dissolve

the precipitate in warm, dilute hydrochloric acid (sp. gr. 1.12), and wash the filter paper until free from iron. Evaporate, with the addition of a little bromine water, until a crust forms, and repeat the basic acetate separation as described above, this time washing the whole of the precipitate onto the filter paper and adding this filtrate to the first one.

The combined filtrates from the two basic acetate separations are evaporated to about 400 cc., and bromine water is added in excess. The solution should be kept hot for an hour, and at the end of this time there still should be a slight odor of bromine. Boil off the excess of bromine and then filter the manganese dioxide, washing with hot water. Dissolve any of the precipitate which may have adhered to the beaker in warm, dilute hydrochloric acid to which a few cubic centimeters of sulphurous acid have been added. Pour this solution through the paper holding the manganese dioxide, and wash the paper with hot water until entirely free from chlorides. Dilute the filtrate to 100 cc., add 10 cc. of disodium phosphate, 10 cc. of ammonium chloride, and *just* enough ammonia to produce a permanent precipitate. Bring the solution to boiling, and boil until the small amount of precipitate appears to have become crystalline. Then add ammonia slowly until it is present in slight excess, and continue to boil, with constant stirring, until the whole of the manganous ammonium phosphate has become silky and crystalline. Allow to stand until cold, filter, and wash with a solution of ammonium nitrate (10 grams NH_4NO_3 in 100 cc. H_2O) which has been made slightly alkaline with ammonia. Dry the precipitate and paper, place in a platinum crucible, and ignite at as low a temperature as possible, taking the same precautions as is usual with the corresponding magnesium ammonium phosphate. The paper should be charred at as low a temperature as possible, and under no circumstances should it be allowed to burn with flame. After it is completely charred the bottom part of the inclined crucible is heated in the oxidizing flame of a Tirrill burner until the precipitate is white.

In the filtrate from the manganese dioxide boil off the bromine, evaporate to about 400 cc., then add to the boiling solution ammonia until slightly alkaline, and ammonium oxalate drop by drop until all of the calcium has been precipitated, finally adding 5–10 cc. in excess. Boil for several minutes, and then allow to stand in a warm place until the precipitated calcium oxalate has completely settled. Decant the solution through a filter paper in such a way that most of the precipitate remains in the beaker. Add a few cubic centimeters of ammonium oxalate to the filtrate to see if precipitation has been complete. Now dissolve the calcium oxalate in the beaker with hydrochloric acid, and pour the solution through the filter, receiving it in a No. 4 beaker and washing with hot water until the washings amount to 250 cc. Heat the solution to boiling, make slightly ammoniacal, add 5 cc. of ammonium oxalate, and allow to stand until the precipitate has completely settled. Pour the clear supernatant liquid through a filter, wash the precipitate twice by decantation with hot water, and then transfer the whole precipitate to the filter and wash until the washings show no test for chloride. Dry the precipitate and paper, place in a platinum crucible, and smoke off the paper with a low flame. After the carbon has all been burned, heat the *covered* crucible with the full flame of a Tirrill burner and finally over the blast lamp to constant weight.

The combined filtrates from the calcium precipitation are evaporated to a volume of 400 cc. If during this evaporation there should be a separation of a white precipitate it will be necessary to evaporate to dryness with concentrated hydrochloric acid. If, however, there is no precipitation add ammonia in excess and di-sodium phosphate, with constant stirring, until precipitation is complete. Allow to stand in the cold (ice water) for several hours, decant the solution through a filter, and wash the precipitate onto the filter with dilute ammonia (three parts H_2O, one part NH_4OH, sp. gr. 0.96), washing several times with this wash water. Now dissolve the precipitate in a small amount of dilute

hydrochloric acid, and wash the paper several times with water. To this solution add 5 cc. di-sodium phosphate, and then neutralize with ammonia, adding it slowly, with stirring, until present in very *slight* excess. After standing 10 minutes, add 10 cc. strong ammonia, sp. gr. 0.90. Allow to stand several hours in ice water, filter, wash with dilute ammonia, and continue until a few drops of the washing, acidified with nitric acid, shows no.turbidity with silver nitrate. Dry the precipitate and paper, and smoke off the filter paper at as low a temperature as possible, being careful not to allow the paper to burn with flame. When charred raise the temperature of heating to the full flame of the Tirrill burner and continue until the precipitate is perfectly white.

DETERMINATION OF COMBINED OXIDES, Fe_2O_3, Al_2O_3, P_2O_5

For the determination of ferric oxide, alumina, and phosphoric anhydride weigh two portions of approximately 0.2 gram each and proceed exactly as in the determination of manganese, calcium, and magnesium, except that the silica which is removed must be treated with hydrofluoric acid, and the residue obtained by this operation must be added to the solution in which iron and alumina are to be determined. To do this, fuse with a small amount of sodium carbonate and dissolve in a small amount of hydrochloric acid.

Instead of making a double basic acetate separation, as was done in the previous case, the second precipitation is made by means of ammonia, and the filtration is made through a closely fitting paper. In washing, care should be taken to thoroughly wash the top of the filter. The filtrate from the basic acetate separation should always be evaporated and examined for iron.

Dissolve the basic acetate precipitate on the filter, and also any which may have adhered to the flask, in hot, dilute nitric acid (sp. gr. 1.20) and wash the paper free from iron. While still warm add ammonia in *slight* excess, allow the precipitate to settle, decant through a filter paper, wash twice by decantation with hot water, and then transfer the

precipitate to the paper and wash several times on the paper with hot, dilute ammonium nitrate solution. Place the washed and dried precipitate in a weighed platinum crucible and smoke off the filter paper at a low temperature. This is best accomplished by inclining the crucible on a triangle and placing a low flame under the front end of it. The flame should be so low that the volatile products will smoke off, but will not ignite. When the paper is completely charred, ignite over the full flame for fifteen minutes and then over the blast lamp for five minutes. During this last heating the crucible remains in an inclined position, with the cover partially covering the mouth, but the oxidizing flame is directed toward the *bottom* of the crucible. Heat to constant weight.

The oxides thus obtained will always contain traces of silica and should be corrected for it. This is done by fusing the oxides with twelve times their weight of acid potassium sulphate until the fusion becomes perfectly clear. After the fusion has become cold it is dissolved in water and the silica is filtered off, washed, ignited, and weighed. This weight subtracted from the weight obtained above gives the true weight of the combined oxides.

DETERMINATION OF IRON IN SPATHIC IRON ORE — ZIMMERMANN-REINHARDT METHOD

Weigh three portions of thoroughly cleaned iron wire, from 0.15–0.25 gram, into 150 cc. Erlenmeyer flasks, and dissolve in 20 cc. of hydrochloric acid (sp. gr. 1.12) and 20 cc. of water. When the solution is complete, add strong potassium permanganate solution drop by drop until the carbonaceous material is completely oxidized and the solution has shown a very marked change of color. Place the flasks on a piece of white paper, and reduce while still hot with the smallest possible volume of freshly-prepared stannous chloride which will produce a colorless solution. If too much has been added it may be corrected by adding potassium permanganate solution until a slight yellow coloration appears, and then adding just enough stannous chloride to reduce the small amount of ferric chloride

present. Cool the solution by holding the flask in running water, and when *cold* add rapidly 10 cc. of mercuric chloride (50 grams per liter). This should produce a very small amount of white, silky mercurous chloride. If there is a large amount formed, or if it is at all dark-colored or flocculent, it is not advisable to try to finish the titration. Wash this solution into 400 cc. of *cold* water to which has been added 10 cc. of manganous sulphate solution (20 grams $MnSO_4$, 220 cc. H_2O, 40 cc. H_2SO_4 — sp. gr. 1.84), and titrate to pink color with potassium permanganate (3 grams per liter) solution which has been filtered through asbestos to remove manganese dioxide.

Potassium permanganate which is to be used in this as well as in other determinations may be standardized accurately against sodium oxalate as follows: Dissolve 0.25–0.30 gram of sodium oxalate in 250 cc. of hot water in a 400 cc. beaker, and add 10 cc. of (1 : 1) sulphuric acid. Titrate with permanganate, stir vigorously, and add the last 0.5–1.0 cc. drop by drop, allowing each drop to be decolorized before adding another. Estimate the excess of permanganate necessary to color the solution by comparing with a similar volume of water and acid. *The temperature of the solution must be maintained throughout the titration between 70–90° C.*

To determine iron in the spathic iron ore weigh two portions of approximately 0.3 gram each into porcelain crucibles. Roast the ore for ten minutes to destroy organic matter, and then dissolve in a small quantity of hydrochloric acid. If there is an insoluble residue it will be necessary to fuse it with a very small quantity of sodium carbonate, take it up in hydrochloric acid, and add it to the main portion. When the solution is complete, reduce with stannous chloride, and then proceed as in the standardization of potassium permanganate against iron wire.

> *Notes.* — 1. Spathic iron ore is essentially ferrous carbonate, but there is always found with it varying amounts of organic matter, silica, alumina, manganese, calcium, magnesium, phosphorus, and sulphur, with traces of titanium.

There is invariably an insoluble residue left after treating with hydrochloric acid, which may contain some or all of these elements. After fusion of the residue with sodium carbonate, solution in hydrochloric acid takes place easily.

A definite amount of sodium carbonate is prescribed, so as to prevent the introduction of an unnecessarily large excess of sodium salts, as would probably be the case if the amount were left to the judgment of the worker.

Four portions are weighed for analysis, because if large enough portions were taken to determine accurately the manganese, calcium, and magnesium there would be difficulty in handling the very bulky precipitate of iron and alumina; consequently smaller portions have been taken for the separate determination of these constituents.

2. The double evaporation of the solution with hydrochloric acid is necessary in order to dehydrate completely all of the silica. This was shown to be true by Hillebrand in the case of silicates, and is even more true here on account of the solvent effect of ferric chloride. This solvent effect is very noticeable if the hydrochloric acid solution is allowed to stand any length of time before filtration.

It is necessary to moisten the dry residue with hydrochloric acid before adding water, because of the strong tendency of ferric and aluminum salts to hydrolyze and form basic salts, which would be filtered off and weighed with the silica. Even when the procedure is carefully followed there is always a slight residue left after the hydrofluoric acid treatment. This residue contains some iron and alumina, and traces of titanium, the latter often being in combination with phosphoric acid.

The treatment with hydrofluoric acid is based on the reaction,

$$SiO_2 + 4HF = SiF_4 + 2H_2O,$$
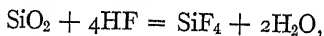
but as there is always the tendency for the silicon tetrafluoride to react with water according to this reaction,

$$3SiF_4 + 4H_2O = 2H_2SiF_6 + Si(OH)_4,$$
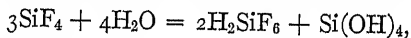
it is necessary to have some sulphuric acid present to remove the water as fast as it is formed. Furthermore, certain other

fluorides, such as those of iron and titanium, are volatilized in the absence of sulphuric acid.

3. The oxidation of the iron to the ferric state is absolutely necessary to the success of the operation. The presence of ferrous iron would not only render the separation incomplete, but it may also cause the formation of the so-called "brick-dust" precipitate, which contains ferrous iron and is extremely difficult to handle. Other oxidizing agents than bromine may be used, but this has been selected, not only on account of its efficiency, but also on account of the ease with which the excess may be removed. If nitric acid is used as the oxidizing agent there sometimes forms, on evaporation, a dark-colored gummy mass, which can only be converted into the crystallized ferric chloride by repeated evaporation with concentrated hydrochloric acid.

The careful evaporation of the excess of hydrochloric acid is to remove the excess of oxidizing agent and to prevent an unnecessary addition of a large quantity of sodium carbonate when neutralizing the ferric chloride solution.

4. Ferric hydroxide possesses, to a very high degree, the property of forming a colloidal solution. When sodium carbonate solution is added to the ferric chloride the ferric hydroxide which is first formed gradually goes into solution in the colloidal state, the increasing amount present being indicated by the solution assuming the deep-red color characteristic of the undissociated iron salts. As the colloidal condition is easily destroyed by heat and the presence of an electrolyte, it is essential to keep the solution cool until ready for use, and under no circumstances should the sodium acetate be added to it before dilution.

The older methods for the separation of iron from manganese were based on the decomposition of this colloidal solution by means of heat in the presence of an electrolyte (Na_2SO_4), which caused a separation of the colloidal ferric hydroxide and the formation of a basic iron salt.

5. The separation of iron and aluminum from the bivalent metals is based upon the relative ease with which the different acetates hydrolyze. The hydrolysis of ferric acetate may be expressed in this way:

$$Fe(CH_3CO_2)_3 + 2H_2O \rightleftharpoons Fe(OH)_2.CH_3CO_2 + 2CH_3CO_2H.$$
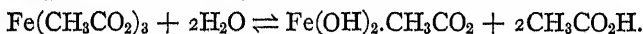
Since hydrolysis is dependent upon the dissociation of water into hydroxyl and hydrogen ions, and as the dissociation is greater at the boiling temperature, the hydrolysis of ferric and aluminum acetates takes place more rapidly and completely at this temperature. Manganese acetate would also hydrolyze somewhat under the same conditions, especially in neutral solution, and it is therefore necessary to diminish the dissociation of water to such an extent that the ferric and aluminum acetates may hydrolyze, but that the manganese acetate may not. This is accomplished by the addition of the weak acetic acid; and in order that it, and also the acetic acid formed in the reaction, may not furnish too great a concentration of hydrogen ions, and thus force the water completely back into the undissociated state, the concentration of hydrogen ions is diminished by the addition of a salt containing an ion in common, viz., sodium acetate. Consequently the strength of the acid is weakened.

If too much acetic acid is used the concentration of the hydroxyl ion is diminished to such an extent that the ferric and aluminum acetates cannot hydrolyze completely. On the other hand, if too little acetic acid or, what is equivalent to the same thing, too much sodium acetate has been used, the concentration of the hydroxyl ion may be so great that the manganese acetate will also hydrolyze and be precipitated with the iron and alumina.

As the reaction involving the hydrolysis is a reversible one, it is evident that in order to force the reaction completely in one direction it is necessary to make the filtration while the solution is still hot. Otherwise some of the precipitate redissolves on cooling.

6. If the process has been properly carried out the filtrate should be clear and colorless, and free from iron. On evaporation any iron which was not precipitated will separate. This, however, should not be confused with the hydrated manganese dioxide, some of which invariably separates during the process of evaporation, the manganous acetate being oxidized by the air.

The best method of deciding whether this precipitate is iron or manganese is to filter it off, dissolve in a small amount of hydrochloric acid, and to make a basic acetate

separation in small volume. If ammonia and ammonium chloride are used the separation may not only be incomplete, but there may be subsequent difficulty in precipitating the manganese in the main filtrate on account of the presence · of ammonium salts.

7. The basic acetate process is the most accurate method for the separation of iron from manganese. For precise work this method should always be used, in spite of some of its disadvantages. It·is also used for the separation of aluminum from the bivalent metals, but for the separation of chromium from the bivalent metals the barium carbonate process is to be preferred. Chromium acetate is incompletely hydrolyzed except in the presence of a very large excess of iron.

In any case where this separation is used phosphoric acid and titanium hydroxide will be precipitated with the trivalent elements.

If it is desired to determine the iron in this precipitate instead of making a determination in a separate sample, it may be done by the process described on page 20.

8. The double separation by means of the basic acetate process is necessary when manganese is to be determined, as there is always some manganese carried down in the first precipitation. This may be partially due to occlusion, but it is also undoubtedly true that in this weakly acid solution some of the manganese is oxidized to the dioxide and carried down in this form.

9. When only iron and aluminum are to be determined, it is believed that a single basic acetate precipitation, followed by a separation with ammonium hydroxide, suffices to give a pure precipitate. The solution in nitric acid must take place before the precipitate has had time to dry. If this precaution is neglected it requires considerably more hot nitric acid to dissolve the precipitate, and in this process the filter paper is more or less attacked. The solution will, therefore, contain enough organic matter to hold the iron and aluminum in solution when ammonia is added. If the recently precipitated hydroxides are dissolved in nitric acid there will be no difficulty in making the ammonia precipitation.

The use of nitric acid has the distinct advantage that it

does away with the tedious washing to remove chlorides; and furthermore, it is easier to keep the iron oxidized to its highest state during the ignition.

Although some of the aluminum hydroxide is probably dissolved in the colloidal form when the final washing is made with pure water, it is believed that this may be largely overcome by making the final washing with dilute ammonium nitrate solution.

10. Bromine separates manganese dioxide from the acetate solution according to this reaction:

$$Mn(CH_3CO_2)_2 + 2Br + 2H_2O = MnO_2 + 2CH_3CO_2H + 2HBr.$$
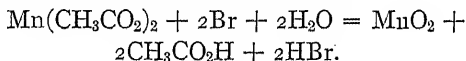
It would seem much simpler to ignite the manganese dioxide and weigh the oxide Mn_3O_4, but this process is open to two serious objections. In the first place, manganese dioxide, when precipitated from solutions containing sodium salts, occludes considerable quantities of sodium; then the composition of the oxide formed on ignition is not always represented by the formula Mn_3O_4. Consequently it is very much more accurate to use the excellent process devised by Gibbs,[1] involving the separation of the manganese as manganese ammonium phosphate, $MnNH_4PO_4$, and its conversion by heat into the pyrophosphate $Mn_2P_2O_7$. Gooch and Austen[2] have carefully studied the best conditions for obtaining a pure precipitate. The precipitate which first forms is the tri-manganic phosphate $Mn_3(PO_4)_2$, but this is converted by heating with an excess of the precipitant and ammonium chloride into the crystalline manganese ammonium phosphate.

The same care which is recommended in Note 13 for the ignition of magnesium ammonium phosphate should be used in this case. If these precautions are neglected there will be some reduction of the precipitate and consequent alloying of the crucible.

11. The double precipitation of the calcium oxalate is absolutely necessary in order to purify it from other salts which it carries down with it. If there is considerable aluminum in the ore it is necessary to ignite the first calcium

[1] *Am. J. Sci.* [2], **44**, 216.
[2] *Am. J. Sci.* [4], **6**, 233.

oxalate precipitate, dissolve the oxides in hydrochloric acid, and to add ammonia in very slight excess to the solution, in order to throw out traces of aluminum hydroxide, which has reached this point in the analysis on account of its having been dissolved in the colloidal form when washing the basic acetate precipitate with water.

Richards [1] has shown that magnesium oxalate is carried down with calcium oxalate, and that the amount of magnesium oxalate occluded is proportional to the amount of undissociated magnesium salt in solution. A double precipitation is therefore always necessary, not only to get a pure precipitate of calcium, but in order to get all of the magnesium into the filtrate.

It is also well known that sodium salts are occluded by calcium oxalate.

12. The first precipitation of magnesium is made simply with the idea of removing it completely from the rest of the solution rather than to get a normal precipitate of the composition represented by the formula $MgNH_4PO_4$. Neubauer [2] has shown that complete precipitation takes place, even in the presence of a large amount of ammonium salts. He has shown, and Gooch and Austen [3] have independently confirmed his results, that a normal precipitate can only be obtained in the absence of ammonium salts and ammonia. To ensure a pure precipitate, the solution must be as nearly neutral as possible, as free as possible from ammonium salts, and ammonia must be added after the addition of the phosphate solution. The large excess of ammonia, as prescribed in most books, is distinctly disadvantageous.

13. The ignition of magnesium ammonium phosphate must be done with extreme caution. If the initial heat is applied too rapidly the ammonia, which is one of the products of the reaction,

$$2MgNH_4PO_4 = Mg_2P_2O_7 + 2NH_3 + H_2O,$$
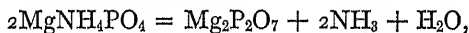
is decomposed, and the hydrogen then attacks the phosphate, reducing it and causing the phosphorus to alloy with the

[1] Richards, McCaffrey and Parker: *Z. anorg. Chem.*, **28,** 71.

[2] *Z. angew. Chem.*, 1896, 435.

[3] *Am. J. Sci.* [3], **7,** 187.

platinum. Heraeus,[1] who has studied this, has shown that this decomposition and reduction take place below 900° C.

14. The Zimmermann-Reinhardt method for the determination of iron has a very distinct advantage because of the possibility of using hydrochloric acid, in which most of the ores are soluble.   The reactions upon which the determination is based are as follows:

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4.$$
$$SnCl_2 + 2HgCl_2 = SnCl_4 + 2HgCl.$$
$$2KMnO_4 + 10FeCl_2 + 16HCl = 10FeCl_3 + 2MnCl_2 + 2KCl + 8HO_2.$$
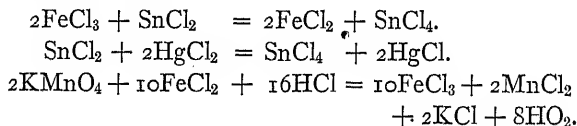
These reactions are practically the same as in the bichromate process for the determination of iron, but the use of potassium permanganate obviates the use of an outside indicator.

By using proper care, just enough stannous chloride can be put in to reduce the iron and to have a very slight excess. If the operation is properly carried out, the precipitate of mercurous chloride is very small in amount and is silky in appearance. If platinum salts have been introduced into the analysis, through an acid potassium sulphate fusion, or through the solution in platinum of an ignited precipitate, it is difficult, and sometimes impossible, to tell when enough stannous chloride has been introduced into the solution. When most of the ferric iron has been reduced, then the platinum begins to be reduced to the platinous form, and, this salt being highly colored, the solution, instead of becoming colorless, as would ordinarily be the case, assumes the red tint of the platinum salt.

15. If too small an amount of hydrochloric acid has been used the stannic chloride, which is one of the products of the reaction, will hydrolyze and give products which interfere with the sharpness of the end point. If too much hydrochloric acid is present it will react with the potassium permanganate, giving high results. Baxter and Frevert [2] have shown that the high results are due to the formation of hypochlorous acid, which escapes from the solution without giving up its oxygen, thus causing an addition of a greater amount of permanganate than would correspond to the actual

[1] *Z. angew. Chem.*, **15,** 917.

[2] *Am. Chem. J.*, **34,** 109.

amount of iron present. This reaction is completely corrected by the addition of a manganous salt, as has been shown by Kessler[1] and by Zimmermann.[2] The mechanism of this reaction is not completely understood, but the evidence points toward the formation of a manganic compound, which reacts with the ferrous iron. In other words, the manganese salt catalyzes the reaction between potassium permanganate and ferrous chloride. On the other hand, in a series of interesting experiments on the oxidation of iron, some evidence has been found that iron is capable of forming a peroxide of the formula Fe_2O_5, which reacts with the ferrous salt. This view, however, would not explain the fact that a manganese salt will accelerate the reaction between potassium permanganate and oxalic acid, causing the reaction to take place in cold solution, while iron salts have no effect upon this reaction.

DETERMINATION OF SULPHUR IN PYRITE

I. AVAILABLE SULPHUR — LUNGE METHOD

Spread out on the bottom of a 200 cc. casserole 0.4 to 0.5 gram of pyrite which has been ground to extreme fineness. Pour over this 20 cc. of a freshly made mixture of three volumes nitric acid (sp. gr. 1.42) and one volume hydrochloric acid (sp. gr. 1.20). Cover the casserole with a watch glass and warm gently until action commences; then remove from the heat until action slackens. Start the action again from time to time and remove from the heat when the oxides of nitrogen begin to be evolved. In this way continue the heating until all action has apparently ceased. Complete disintegration should be accomplished in five to ten minutes. If sulphur separates it is probable that the reaction was allowed to proceed too violently, or that the pyrite was not ground finely enough. In case sulphur has separated it is preferable to start with a new sample rather than to try to oxidize the separated sulphur by the addition of potassium chlorate.

[1] Z. anal. Chem., 1, 329.
[2] Berichte, 14, 779.

When disintegration is complete add 5 cc. of sodium carbonate solution, and evaporate to dryness on the steam bath. Pour over the dry mass 5 cc. of hydrochloric acid (sp. gr. 1.20) and again evaporate to dryness. Moisten the residue with 1 cc. of concentrated hydrochloric acid, warm gently for a moment, then dilute with 100 cc. of hot water. Filter, wash several times with hot dilute hydrochloric acid, and finally with hot water.

Pour the filtrate into a slight excess of ammonia and keep the mixture hot for ten or fifteen minutes. Filter through a 4-inch Swedish paper, wash first by decantation, and then, throwing the precipitate onto the paper, wash thoroughly with hot water.

If the filtrate and washings exceed 250 cc., acidify with hydrochloric acid and concentrate to approximately this volume. To the boiling, slightly acid solution add a hot solution of 5 per cent barium chloride from a dropper, allowing the drops to run down the inside of the beaker until a slight excess has been added. Allow to stand in a warm place for half an hour, filter, washing by decantation with hot water until the washings are free from acid, and then complete the washing on the filter until free from chlorides.

When the filter has drained as much as possible from wash water, fold it over the barium sulphate, and place it in the bottom of a weighed platinum crucible. Incline the crucible on its side, with the lid partially covering the front, and place under the front end a flame so small that it will dry the paper so slowly that there is no danger of spattering, and that it will char the paper without having it take fire. When the paper is completely charred, place under the back of the crucible the full oxidizing flame of a Tirrill burner, and heat thirty minutes. As some of the barium sulphate is invariably reduced to sulphide, it is necessary to allow free access of air into the crucible, and to continue the heating until constant weight is obtained.

II. AVAILABLE SULPHUR — METHOD OF ALLEN AND BISHOP [1]

1.3736 grams of the dried ore are put in a dry 300 cc. Jena beaker, 10 cc. of a mixture of 2 parts by volume liquid bromine and 3 parts carbon tetrachloride are added and the beaker is covered with a watch glass. After standing 15 minutes at room temperature with occasional gentle shaking, 15 cc. nitric acid (sp. gr. 1.4) are added and the mixture is allowed to stand fifteen minutes longer at room temperature with occasional shaking. The beaker is then placed on an asbestos board on top of the steam bath and allowed to remain there until all action has ceased and most of the bromine has been volatilized. It is then placed within the rings of the bath and the solution evaporated to dryness, the cover glass being raised above the rim of the beaker by means of riders made of bent glass rods. Ten cc. hydrochloric acid (sp. gr. 1.2) are next added, and, after shaking to mix thoroughly, the solution is again evaporated to dryness, still keeping the beaker covered as in the former evaporation. When completely dry the silica is dehydrated by heating in an air bath at 100° C. for several hours.

Four cc. of hydrochloric acid (sp. gr. 1.2) are now added to the dehydrated mass, followed after five minutes by 100 cc. of hot water. The cover, sides of beaker, and riders are care- fully washed down with hot water and after the removal of the riders the cover is replaced. The mixture is gently boiled for five minutes to insure complete solution of all sulphate. After the solution has partially cooled by standing for about five minutes, 0.2 to 0.3 gram of powdered aluminum is added and the beaker gently stirred until the iron color has disap- peared, showing complete reduction. It is now advisable to cool the solution to prevent possible mechanical loss of material in the form of mist when filtering, due to the action of warm hydrochloric acid on the excess of alumi- num powder. After cooling, the cover glass and sides of

[1] *Eighth International Congress of Applied Chemistry*, **1**, 33; *J. Ind. Eng. Chem.*, **8**, 1167.

the beaker are washed down and the solution is filtered through an 11 cm. filter paper into a No. 7 beaker and the residue washed nine times with hot water. To the filtrate are added 3 cc. more of hydrochloric acid (sp. gr. 1.2) and sufficient cold water to dilute to 800 cc. After stirring to mix well, the beaker is covered with a large clock glass and the sulphate precipitated by adding through a special form of "precipitating cup" (discharging at the rate of 5 cc. per minute) 50 cc. of 5 per cent barium chloride solution. The solution is *not* stirred while the barium chloride is being added but after all is in, the supernatant liquor is mixed by gentle stirring.

After the barium sulphate has settled it is filtered through a tared Gooch crucible, using suction. The Gooch crucible used has a capacity of 35 cc., with perforated bottom attached, and with a moderately thick asbestos mat. The clear liquid is siphoned through the crucible, the precipitate is transferred to the filter by a stream from a wash bottle, and the beaker washed six times with cold water. The crucible is then ignited slowly, placing it first on an asbestos board over a flame for 25 minutes so as to expel the water gradually, or it may be given this preliminary drying by placing it in the steam oven for a few hours if more convenient. The crucible is then heated with the full flame of a Tirrill burner for thirty minutes, cooled in a desiccator, and weighed.

III. TOTAL SULPHUR — FRESENIUS METHOD

Mix 0.4 to 0.5 gram pyrite with ten parts of a mixture of four parts sodium carbonate and one part potassium nitrate in a platinum crucible.

Cut an opening in an asbestos board (at least 4 inches square) sufficiently large to allow the lower two-thirds of the crucible to project below the board. Place the covered crucible in this opening, heat gently at first, and finally raise the temperature enough to bring the mass to fusion. Any unnecessary increase in the heat should be avoided on account of the action of the oxidizing mixture on the platinum. Keep

the mass in fusion fifteen minutes, stirring, if necessary, with a stout platinum wire to prevent the fusion from caking on the sides of the crucible.

When the action has apparently ceased, place the crucible in a porcelain casserole, and extract the residue several times with boiling water. Decant the solution through a filter paper and then boil the residue with 20 cc. of a 10 per cent solution of sodium carbonate. Finally, wash the residue thoroughly with a 1 per cent solution of sodium carbonate.

Make the filtrate distinctly acid and add 5 cc. of hydrochloric acid (sp. gr. 1.20) in excess. Boil to expel the carbon dioxide and evaporate to dryness. Moisten the residue with 5 cc. concentrated hydrochloric acid and again evaporate to dryness. Then warm the residue gently with 2 cc. of hydrochloric acid (sp. gr. 1.20) and add 100 cc. of hot water; filter, and wash the silica.

In the filtrate, which should amount to about 250 cc., the sulphuric acid is precipitated in boiling solution by hot barium chloride, as in the Lunge method, and the barium sulphate should be filtered, washed, and ignited in the same manner.

IV. TOTAL SULPHUR — SODIUM PEROXIDE METHOD [1]

Mix about 0.5 gram of pyrite with 5 grams sodium peroxide and 4 grams sodium carbonate in an iron crucible. Place the crucible in an opening cut in an asbestos board, heat gently for ten minutes and then raise to the full heat of a Tirrill burner for 25 minutes. Allow the crucible to cool, place in a casserole containing 150 cc. of water, digest until the sodium salts are dissolved. Remove the crucible, wash with hot water, and to the solution add 5 cc. of hydrochloric acid (sp. gr. 1.20) which has been saturated with bromine. Heat to boiling, filter the ferric hydroxide, and wash free from sulphate. Acidify the filtrate with hydrochloric acid, evaporate to dry-

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[1] Hempel, *Z. anorg. Chem.*, **3**, 193; Clark, *J. Chem. Soc.*, **63**, 1079; Glaser, *Chem. Ztg.*, **18**, 1448.

ness to remove silica, take up in 2 cc. of hydrochloric acid (sp. gr. 1.20) and add 100 cc. of hot water; filter and wash.

In the filtrate, precipitate the sulphate and proceed exactly as in the Fresenius method.

Notes. — 1. The very great commercial importance of pyrite makes the accurate estimation of sulphur one of the most important determinations in the whole field of analytical chemistry. For the determination of *available* and *total* sulphur, the methods of Lunge and Fresenius, respectively, are undoubtedly the most accurate. The Lunge method determines only that portion of the total sulphur which is available for the manufacture of sulphuric acid; the Fresenius method determines all of the sulphur irrespective of the form in which it exists. Very many other methods have been proposed, but none of them has met with such general favor as these two, and they can at this time be considered as standards for this determination.

2. The Fresenius method has the disadvantage that the oxidizing flux attacks the platinum crucible badly and, furthermore, it is always necessary to completely destroy the nitrate before precipitating the sulphate ion. It has been repeatedly demonstrated that the sodium peroxide method gives entirely satisfactory results, and it has the advantage of being more rapid than the Fresenius method. Occasionally the water extract of the fusion shows the presence of manganate or permanganate and this may be destroyed by the addition of a few drops of alcohol.

3. If the reaction in the Lunge method is allowed to begin too vigorously there is invariably a separation of sulphur, and, while it is possible to oxidize the separated sulphur, it is only done at the expense of much time and after the addition of considerable potassium chlorate.

The Lunge method cannot be used for the decomposition of many of the native sulphides on account of the strong tendency of some of them to liberate their sulphur in the free state. By using pure fuming nitric acid, or by reversing the proportions of nitric and hydrochloric acids, the decomposition and oxidation of most sulphides may be accomplished successfully.

The Allen and Bishop method has the advantage over the Lunge method in that it efficiently takes care of separated sulphur. The carbon tetrachloride dissolves the sulphur immediately on its separation and it is then oxidized by the bromine also held in solution by this solvent.

4. It is necessary in all cases, before precipitation of barium sulphate, to remove completely all traces of nitric or nitrous acids by repeated evaporation with hydrochloric acid. It was shown as early as 1842 by Mitscherlich that barium sulphate carried down many salts from solution; on the other hand, its complete precipitation is inhibited by the presence of certain salts. In either case, when an accurate determination of sulphur is to be made, the salts which interfere with the precipitation must be removed before barium chloride is added to the solution. Among the more common substances which are carried down with barium sulphate are the chloride, nitrate, and chlorate of barium, sodium, and potassium; copper, zinc, iron, and aluminum salts. Some interesting experiments have been made by Hulett and Duschak,[1] showing the amounts of barium chloride actually carried down with the barium sulphate. They have also devised a very simple method by which corrections can be made for this error. The complete precipitation of all of the sulphuric acid in solution is interfered with by the presence of chromium salts, metaphosphoric acid, etc.

5. The precipitation of barium sulphate in the presence of ferric iron has received attention from a large number of investigators. It has been known for a long time that low results are obtained when barium sulphate is precipitated from solutions containing ferric iron, notwithstanding the fact that the precipitate is contaminated with ferric oxide. In the process of ignition sulphur trioxide is lost, and the amount lost more than counterbalances the weight of the ferric oxide. The old method of fusing the ignited precipitate, if it showed a red color, led to inaccurate results, although insuring a purer precipitate. Some of the sulphuric acid was always lost during the process of ignition, the amount depending upon the time and temperature of heating.

Various remedies have been proposed in order to overcome

[1] *Z. anorg. Chem.*, **40**, 196.

the difficulty of the precipitation of barium sulphate in the presence of iron salts. These remedies may be classed under three heads:

(1) Removal of the iron before precipitation.
(2) Conversion of the ferric ion into a complex ion.
(3) Conversion of the ferric ion to the ferrous ion.

The Fresenius method is the best representative of the first principle. In this case the iron is completely removed as the oxide, and, after the subsequent removal of nitrous and nitric acids by evaporation with hydrochloric acid, the precipitation may be carried out under the most favorable conditions.

In the Lunge method this same result is reached by pre-cipitation of the iron by means of ammonia. Many chemists have claimed that this precipitation of ferric hydroxide always gave inaccurate results on account of the retention of basic iron sulphate in the ferric hydroxide precipitate. Lunge has repeatedly expressed the firm conviction, however, that if the method is carried out as he directs there will be no loss on this account. Gladding [1] modified the method so as to obviate the tedious washing of the ferric hydroxide precipi-tate. He recommended redissolving the ferric hydroxide in hydrochloric acid and then adding barium chloride to this solution to recover the small amount of sulphuric acid carried down.

The most interesting modification of the Lunge method involving the same principle is that of Küster and Thiel.[2] They advised the precipitation of the ferric ion by an excess of ammonia and the addition of barium chloride to this solu-tion, dissolving the ferric hydroxide after the complete pre-cipitation of the barium sulphate. This method overcomes the objection raised by Gladding, in that it removes the iron from solution, and furthermore it does away with a trouble-some filtration. The results obtained by this method are un-doubtedly higher than those obtained by the Lunge method. Whether or not this is due to a certain counterbalancing of errors remains to be seen after further experiments have

been tried. It is highly probable that the occlusion of barium chloride by the precipitation of the barium sulphate in the ammoniacal solution would be considerable. Lunge[1] has admitted and shown by a series of experiments that his own method gives accurate results only because of a counter-balancing of errors.

The conversion of the ferric ion into a complex ion was first suggested by Jannasch and Richards,[2] who used for this purpose formic, acetic, and citric acids, and this was extended by Küster and Thiel,[3] who used oxalic and tartaric acids; but in neither case were the results entirely satisfactory, as the precipitates were invariably colored by occluded iron.

The conversion of the ferric into the ferrous ion also originated with Jannasch and Richards,[4] but the results by this method have not been entirely satisfactory. When zinc and hydrochloric acid are used for the reduction, the zinc in solution is always carried down by the barium sulphate. In the hands of some chemists this method has been more satisfactory, although it has not come into general use.

No completely satisfactory explanation has yet been offered as to why barium sulphate carries down iron salts nor why solutions containing iron salts will retain some barium sulphate. Some evidence has been offered by Jannasch and Richards[5] for the existence of a barium ferric sulphate, and this idea has been subjected to experimental study by Schneider,[6] who came to the conclusion that a solid solution of low concentration was formed. On the other hand, Ostwald[7] has called attention to the analogy with chromium salts, which on heating form a complex ion containing the SO_4 group, which does not react with barium ions. Küster and Thiel[8] developed this idea and assumed that some such complex as $Ba[Fe(SO_4)_2]_2$ is formed, but they admit from the data at hand that it is impossible to say what the

[1] Z. angew. Chem., 1904, 913; 1905, 1921.

[2] J. prak. Chem., 147, 325.

[3] Z. anorg. Chem., 19, 97.

[4] J. prak. Chem., 147, 322.

[5] J. prak Chem., 147, 332.

[6] Z. phys. Chem., 10, 425.

[7] Z. phys. Chem., 29, 340.

[8] Z. anorg. Chem., 25, 322.

nature of the complex is. It seems probable that the true explanation will be that barium sulphate is capable of forming a solid solution with some product of the hydrolysis of ferric sulphate.

6. The explanation of the occlusion of barium chloride is very much more satisfactory. Hulett and Duschak have carefully determined the amounts of barium chloride carried down by barium sulphate under varying conditions, and have offered an explanation of this occlusion which seems to be satisfactory. They have found that barium sulphate carefully washed and dried at 140° contains not only barium chloride, but also chlorine in some form of combination which splits off hydrochloric acid at higher temperatures. Reasoning by analogy, they assume that barium chloride may, like lead and mercuric chlorides, dissociate not directly into Ba and Cl ions, but the dissociation may take place in this way:

$$BaCl_2 \leftrightarrows BaCl^{\cdot} + Cl'$$
$$BaCl^{\cdot} \rightleftarrows Ba^{\cdot\cdot} + Cl'.$$
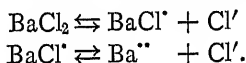
In like manner sulphuric acid also dissociates:

$$H_2SO_4 \rightleftarrows HSO_4' + H^{\cdot}$$
$$HSO_4 \leftrightarrows SO_4'' + H^{\cdot}.$$
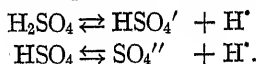
On the assumption of such partial dissociation, $BaCl^{\cdot}$ ions could combine with HSO_4' ions to form the salt $BaCl^{\cdot}HSO_4$, which, upon being sufficiently heated, would split off hydrochloric acid and leave neutral $BaSO_4$. Hulett and Duschak also assumed the possibility of such reactions as the following taking place:

I. $\quad 2BaCl^{\cdot} + SO_4'' \rightleftarrows \begin{matrix} BaCl \searrow \\ BaCl \nearrow \end{matrix} SO_4.$

II. $\quad 2HSO_4' + Ba^{\cdot\cdot} \rightleftarrows \begin{matrix} HSO_4 \searrow \\ HSO_4 \nearrow \end{matrix} Ba.$
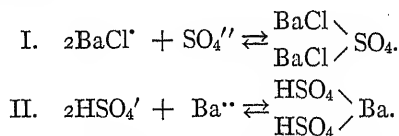
When the salt $\begin{matrix} HSO_4 \searrow \\ HSO_4 \nearrow \end{matrix} Ba$ is heated it should give off sulphuric acid and leave barium sulphate; when heated together with more than the equivalent of $\begin{matrix} BaCl \searrow \\ BaCl \nearrow \end{matrix} SO_4$, hydrochloric acid should form; and when heated with less than the equivalent, then we should expect both hydrochloric and sulphuric

acids. This condition was actually realized by Folin,[1] who studied the conditions under which either one or the other of these two salts should form. He also suggested the possibility of formation of salts of the character represented by the formula $\begin{matrix} M' \, SO_4 \searrow \\ M' \, SO_4 \nearrow \end{matrix}$ Ba in which M represents any metal. This would account for the carrying down of potassium when barium sulphate is precipitated in its presence.

7. Too long and too high heating of the fusion in the Fresenius method will cause considerable attack upon the platinum crucible, and consequently the introduction of platinum into the analysis. If other constituents than sulphur are to be determined, this fact must be taken into consideration, and the platinum removed accordingly.

The completeness of the reaction may be judged by the appearance of the residue after fusion. It should have the color of rouge. If black, it will contain ferrous sulphide.

The use of coal gas for heating the crucible is almost unavoidable in a large laboratory, but in small laboratories the use of an alcohol lamp is strongly advised. The deflection of the products of combustion by means of an asbestos board partially overcomes the difficulty.

That barium sulphate is easily reduced to sulphide during the process of ignition is not sufficiently recognized. As much care should be used in the ignition of this precipitate as in the ignition of magnesium ammonium phosphate.

It should also be remembered that under no circumstances is it permissible to heat barium sulphate over the blast lamp. Above 900° it loses sulphur trioxide, and the residue becomes alkaline, owing to loss of sulphur trioxide.

DETERMINATION OF TITANIUM IN TITANIUM IRON ORE

I. METHOD OF GOOCH [2]

Fuse 0.4–0.6 gram of finely-ground ore with 6 to 8 times its weight of sodium carbonate until action ceases. Extract the mass with hot water, and decant the solution through a

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[1] *J. Biol. Chem.*, I, 131.

[2] *Chemical News*, 52, 55, 68.

filter. Boil the residue with 25 cc. of sodium carbonate solution, filter, and then wash the residue on the filter paper several times with dilute sodium carbonate solution. Place the filter and residue in a platinum crucible, and ignite at a low temperature until the filter paper is burned. Fuse with 12 to 15 parts of dry potassium pyrosulphate for one-half hour. The temperature of the fusion should be so regulated that the mass is kept in the molten condition, but sulphur trioxide should escape only when the lid of the crucible is removed. Cool, and remove the fusion from the crucible by means of a platinum wire. Suspend the fusion in 200 cc. of *cold* water, to which has been added 100 cc. of sulphurous acid, and allow to stand in a cool place until solution is complete.

Filter if necessary. To the solution add 125 cc. of acetic acid (sp. gr. 1.04), and dilute to 800 cc. in a liter beaker. Add 20 grams of ammonium acetate dissolved in a small amount of water and boil from 3 to 5 minutes, adding, just before the boiling point is reached, an additional 25 cc. of sulphurous acid. Allow to stand in a warm place for one-half hour and then filter, by means of a siphon, through a 9 cm. paper.

Wash the precipitate with five per cent acetic acid solution until most of the sulphate has been removed, and then ignite the paper and precipitate at a low temperature. Fuse with potassium pyrosulphate again. Proceed exactly as before, finally igniting to constant weight and weighing the precipitate as TiO_2.

Notes. — 1. Titanium iron ore is essentially ferrous titanate of the composition represented by the formula $FeTiO_3$, but it rarely occurs in this form except in isolated crystals. In the massive form it approximates this composition, but it is always contaminated with silica, phosphorus, alumina, manganese, calcium and magnesium. It is of small importance at the present time as an iron ore, but it is the source from which ferro-titanium, an increasingly useful product, is obtained.

2. As some of the titanium ores are very refractory and do not yield to treatment with acids, special methods have been

devised, not only for getting the ores into solution, but also for some of the separations necessary. Even if the ore proved to be acid soluble, silica cannot be removed by the usual process of evaporation to dryness, on account of the formation of insoluble compounds containing phosphorus and titanium. It is, therefore, customary to remove silica and phosphorus together by fusing the ore with sodium carbonate. The silicate and phosphate of sodium are leached out and removed from the insoluble sodium titanate, ferric oxide, and carbonates of the alkaline earths. Some of the aluminum goes into the filtrate, and part remains in the residue.

3. Ignition of the sodium titanate residue must be made at a low temperature, as it becomes less soluble on prolonged or high heating.

4. Fusion of any substance with potassium pyrosulphate requires considerable skill, patience and caution. The preliminary heating should be carried out slowly and at a low temperature, on account of the tendency to froth over, which always results in the loss of the determination, and sometimes in serious burns. To avoid as far as possible the frothing, which is most vigorous during the first part of the heating, potassium pyrosulphate should be used, and not the acid potassium sulphate. The former may easily be made by heating the latter to fusion for a very short time. Prolonged heating leads to the formation of the normal sulphate.

It is an inexcusable mistake to try to hurry the solution of the sulphate fusion by heating. Hydrolysis invariably takes place, with the formation of a colloidal solution.

5. The separation of titanium from iron, aluminum and manganese is based upon the same principle involved in the separation of iron and aluminum from manganese, as given under the Analysis of Spathic Iron Ore.[1] The iron is prevented from hydrolyzing by being kept in the ferrous condition, and the aluminum and manganese are prevented by having a hydrogen ion concentration so great that they will not hydrolyze, but titanium may hydrolyze completely, and precipitate.

Titanium will hydrolyze completely on continued boiling from strong acid solutions, but it usually separates in such a

[1] Page 23, note 5.

form as to make its filtration difficult, if not impossible. If the directions are carefully followed, titanium hydroxide should separate quickly and in a flocculent form which filters with comparative rapidity.

6. Separation of iron and titanium by this method is usually complete, although a second precipitation is necessary. Other methods for the separation of these two elements have been recommended, the most promising of which depends upon the solubility of ferric chloride in ether.

7. Colorimetric estimation of titanium,[1] when present in small amounts, is not only rapid, but very accurate. The method is based upon the reaction which takes place between titanium salts and hydrogen peroxide. The intense yellow color produced is compared with standards of known titanium content.

II. METHOD OF BARNEBY AND ISHAM [2]

The weighed sample, 0.4–0.6 gram, is moistened in a platinum crucible with a few drops of water, 5–10 drops of concentrated sulphuric acid and 1 cc. of hydrofluoric acid are added. The crucible is heated as in the removal of silica until the complete removal of sulphur trioxide. Five grams of sodium carbonate and a little sodium nitrate are added and the mixture fused for 30 minutes. After cooling, the crucible is placed in a beaker, covered with hot water, and heated until the melt is disintegrated. The residue is filtered and washed with hot water. The filter is perforated and washed with hydrochloric acid (sp. gr. 1.11) into a clean beaker, and any residue in the crucible is dissolved and added to this solution. The beaker is heated until solution is complete and until the volume is reduced to 15–20 cc. After cooling the solution is transferred to a separatory funnel, the beaker being washed with hydrochloric acid (sp. gr. 1.11). An equal volume of ether, which has been shaken with concentrated hydrochloric acid, is added, the funnel inverted and shaken, releasing the pressure at intervals by opening the stop-cock, and allowing

[1] *U. S. Geol. Survey, Bulletin* 422, 128.
[2] *J. Am. Chem. Soc.*, **32**, 957.

the liquid carried up by the escaping vapor to run back before closing the stop-cock. The funnel is then allowed to stand in an upright position for 10 minutes, and then the aqueous layer is drawn off into another separatory funnel. The ether is rinsed twice by shaking with 5–10 cc. portions of hydrochloric acid and the washings added to the aqueous solution. The treatment with ether is repeated until the ether layer no longer shows the greenish tinge of dissolved ferric chloride. The aqueous solution is then transferred to a beaker, 10 cc. of concentrated sulphuric acid are added and the solution evaporated to fumes of sulphur trioxide. The cooled solution is diluted to about 100 cc. and nearly neutralized with ammonia. Two grams of ammonium bisulphite are added and the solution warmed for one-half hour. Ten grams of ammonium acetate and 5–10 cc. of glacial acetic acid are added and the solution boiled for 15 minutes. Filter, wash with dilute acetic acid, ignite and weigh as TiO_2.

Notes. — 1. The method is based on the removal of silica with hydrofluoric acid, the removal of phosphates, sulphates, and aluminates by fusion with sodium carbonate and extraction with hot water, and the removal of the iron by extraction of the ferric chloride with ether. The titanium is then hydrolyzed as in the preceding method in the presence of an acetate and acetic acid.

IODIMETRIC DETERMINATION OF COPPER

MODIFIED METHOD OF A. H. LOW [1]

Standardization of Sodium Thiosulphate Solution. — Prepare a solution of sodium thiosulphate by dissolving about twenty-five grams of the salt in one liter of water, which has been recently boiled and cooled out of contact with the air. Weigh accurately two portions of about 0.25 gm. of pure, clean copper wire into 250 cc. Erlenmeyer flasks, and dissolve in a mixture of 5 cc. concentrated nitric acid and 25 cc. of water. When solution is complete, heat to boiling, add 5 cc. of bromine water

[1] *J. Am. Chem. Soc.*, **24**, 1082.

continuing the boiling until the bromine is expelled. Allow to cool, add a *slight* excess of strong ammonia, and boil the solution until the excess has been driven off. This point is indicated by the change in color of the solution, or by a slight precipitation of copper hydroxide. Add a few cubic centimeters in excess of strong acetic acid and boil if necessary to dissolve any copper hydroxide. Cool to room temperature, add three grams of potassium iodide, dissolved in a small amount of water, and titrate at once with the sodium thiosulphate solution. When the brown color of the iodine has become weak, add enough starch solution to give a distinct blue color, and finish the titration by adding sodium thiosulphate slowly until the color due to the free iodine has completely disappeared.

Work slowly toward the end point and stop short of complete decolorization, and then continue only when the liquid after standing a minute or two, still persists in a tinge of color.

Procedure. — To 0.25–0.50 gram of finely ground ore weighed into a 250 cc. Erlenmeyer flask, add 6 cc. of nitric acid (sp. gr. 1.42) and heat gently nearly to dryness. Add 5 cc. of strong hydrochloric acid and heat again. As soon as the incrusted matter has dissolved, add 7 cc. of concentrated sulphuric acid and heat until the sulphuric acid fumes freely. Cool, and add 25 cc. of water. Then heat until any anhydrous ferric sulphate is dissolved, and filter to remove insoluble sulphates and silica. Wash the flask and filter paper until the volume of the filtrate amounts to about 75 cc., receiving it in a No. 2 beaker. Place on its edge in the beaker a piece of sheet aluminum, 2 in. x 6 in., bent into triangular shape. Cover the beaker and boil gently for seven to ten minutes, which will be sufficient to precipitate all the copper provided the solution does not exceed 75 cc. Avoid evaporating to very small bulk. The aluminum should now appear clean, the copper being detached or loosely adhering. Remove from the heat and wash down the cover and sides of the beaker with hydrogen sulphide water. Decant the liquid through a filter and then without delay transfer, by means of a jet of hydrogen sulphide water

from a wash bottle, the copper to the filter, leaving the foil as clean as possible in the beaker. Wash the copper and filter thoroughly with hydrogen sulphide water, being careful not to allow the filter to stand empty until the washing is finished. Place the original flask under the funnel and pour over the aluminum in the beaker 5 cc. of a mixture of equal parts of concentrated nitric acid and water. Heat just to boiling and pour the hot acid very slowly upon the filter, lifting the fold if necessary. Now, before washing, pour 5 cc. of bromine water into the filter and wash the beaker and filter with hot water. Finally, remove the filter and wash any residue upon it into the flask. If the bromine was not sufficient to give a slight tinge to the filtrate more of it must be added. Boil the filtrate, which does not exceed 75 cc. to expel the excess of bromine but do not concentrate to small volume. Remove from the heat and add a slight excess of strong ammonia (usually 7 cc.). Boil off the excess of ammonia and add 3 or 4 cc. of strong acetic acid. Cool to room temperature, add three grams of potassium iodide, dissolved in a small amount of water and titrate with thiosulphate as in the standardization.

Notes. — 1. The principle of this method is based upon the fact that when potassium iodide is added to a weakly acid solution of a copper salt iodine is liberated according to this equation:

$$2(CH_3COO)_2Cu + 4KI = Cu_2I_2 + 4CH_3COOK + I_2.$$
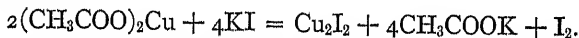
The iodine is then made to react with standardized sodium thiosulphate according to the reaction:

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6.$$
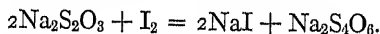
2. Copper ores contain varying amounts of silica, sulphur, arsenic, antimony, lead, silver and iron, and the method is so designed as to remove or render these elements inert.

Nitric acid is the best solvent for sulphide ores and in order to dissolve oxides of iron, remove silver, lead and silica hydrochloric and sulphuric acids are used simultaneously. Complete solution of anhydrous ferric sulphate must take place previous to the filtration of silica, silver chloride and lead sulphate.

3. Aluminum·foil precipitates copper from its solution quickly and completely provided the proper concentration of acid has been obtained. In addition to copper, lead, silver, bismuth, arsenic and antimony may be precipitated if present. Lead should, however, have been almost completely removed as insoluble sulphate, and silver as chloride. The presence of lead and bismuth have no effect upon the analysis except for a slight change of color due to the presence of their slightly colored iodides.

Arsenic and antimony would interfere if allowed to remain in the lower state of oxidation by reacting with the liberated iodine. Consequently the nitric acid solution is treated with bromine to oxidize these elements to the higher state of oxidation. Bromine also oxidizes any nitrous acid which might be in the solution as the result of the reaction between copper and nitric acid.

4. Hydrogen sulphide water is used not only to precipitate traces of copper left in solution, but also to prevent oxidation of finely divided copper.

5. The addition of ammonia and acetic acid is for the purpose of regulating the hydrogen ion concentration. In the presence of strong acids there is danger of hydriodic acid reducing arsenic and antimonic acids with the liberation of free iodine. This reaction takes place so very slowly in the weak acid solution that the effect is negligible.

The presence of much ammonium acetate interferes with the sharpness of the end point, due to the oxidizing action of iodine upon the ammonia from the hydrolyzed ammonium acetate.

6. The amount of potassium iodide added is in excess of that required for 0.50 gram of copper and consequently should be enough to take care of all ores on the weight of sample specified. The reaction proceeds slowly unless an excess is present. An excess beyond a certain limit has no effect upon the analysis, and this excess must be controlled in accordance with the volume of the solution.

The reaction takes place in the presence of sulphuric and hydrochloric acids as well as in acetic acid solution, but on account of the greater hydrogen ion concentration in the two former acids, the volume of the solution must be more care-

fully regulated in order to prevent reaction between the acid and potassium iodide. Gooch and Heath[1] have studied the effect of concentration upon this reaction for sulphuric, hydrochloric, nitric and acetic acids.

7. Standardized solutions of sodium thiosulphate and iodine are both fairly stable if properly prepared from pure materials and protected from light and heat. Water free from carbon dioxide should be used for the solution of the sodium thiosulphate, otherwise there is separation of free sulphur. Both solutions should, however, be frequently checked against each other and against some standard. Copper is used in this case as the standard as it is easily obtained in pure form, and further it reproduces all of the conditions obtained during the course of the analysis. In this connection it is well to refer to the method given on page 83, for the standardization of sodium thiosulphate.

PROXIMATE ANALYSIS OF COAL[2]

Moisture. — A one gram air-dried sample is weighed into a shallow porcelain capsule $\frac{7}{8}$ inch deep and $1\frac{3}{4}$ inches in diameter, and heated for one hour at 105° in a constant temperature oven, through which a current of air, dried by passing through sulphuric acid, is passing at a rate to change the total volume of air in the oven two to four times a minute. The covered capsule is cooled in a desiccator over sulphuric acid and weighed. The loss in weight is called "moisture at 105°."

Ash. — The determination is made upon the same sample in which moisture has been determined. The capsule containing the sample is heated at a low temperature obtained by placing it above the tip of a flame turned down to 2 or 3 inches in height. The sample should be stirred frequently with a stout nichrome wire. After much of the carbon has been burned off the temperature should be gradually raised to about 750° C. and the heat continued at this temperature for

[1] *Am. J. Sci.* [4], 24, 67.

[2] *Technical Paper 76, Bureau of Mines* 1914; *Am. Soc. for Testing Materials* (1914).

30 minutes, or until all of the carbon is burned off. Cool in a desiccator and weigh. The residue represents the "uncorrected ash."

Volatile Matter. — One gram of coal is weighed into a platinum crucible which is provided with a tightly fitting perforated nickel cover. The crucible is placed in the flame of a Meker burner and heated for *seven* minutes to 950° C. After the more rapid early discharge of the volatile matter, tap the crucible cover so as to seal the cover and crucible more perfectly. The temperature should be determined by means of a thermo-couple placed through the cover, and touching lightly upon the bottom of the crucible. Cool the crucible in a desiccator and weigh. The loss in weight minus the moisture at 105° C. represents the volatile matter.

Fixed Carbon. — The fixed carbon is obtained by subtracting the sum of the percentages of moisture, ash and volatile matter from 100.

Sulphur. — Mix thoroughly on glazed paper 1 gram of coal and 3 grams of Eschka mixture (two parts of magnesium oxide and one part of sodium carbonate), transfer to a porcelain crucible, or a platinum crucible, and cover with 1 gram of Eschka mixture. Heat the crucible at a low temperature for 30 minutes with an alcohol flame or in an electrically heated muffle furnace, and then raise the temperature to about 925° C. for one hour or until all of the black particles of carbon disappear.

Transfer to a 300 cc. beaker and digest with 100 cc. of hot water for one-half hour. Filter, wash by decantation several times and finally transfer the residue to the filter paper and wash. Treat the filtrate amounting to about 250 cc. with 10 cc. saturated bromine water, acidify slightly with hydrochloric acid and boil off the excess of bromine. To the boiling solution add hot dilute barium chloride and proceed as in the determination of sulphur in pyrite.

Notes. — 1. The proximate analysis of coal originated in response to a demand for a rapid, fairly accurate method for classifying coals for industrial purposes. The results give

important data as to the commercial value, and may be obtained in very much shorter time than the results of an ultimate analysis.

2. The sampling of coal, whether at the mine or at the place of destination, is a very important matter, and the subject is too extensive to be dealt with here. The student should read on this subject the papers referred to on page 47.

3. The loss of weight at 105° includes not only that moisture which is adsorbed on the surface, but also some of the water which is an essential part of the coal itself. Samples may have been taken from a wet face of the mine or from a car which had been standing in the rain or snow, and the amount of this moisture varies with the weather conditions. It is, therefore, desirable to establish nearly normal conditions by air-drying the sample. Coal exposed to circulating air at ordinary temperatures will either give up or take on moisture depending upon the fineness of the sample and the humidity of the air. A point of equilibrium is always reached which varies with the size of the lumps of coal exposed, the time of exposure and the humidity of the air.

The inherent moisture or water of constitution varies fairly constantly with the district from which the coal is taken. The coal from the more important veins of the Appalachian field holds about 2–4 per cent of moisture; that from the western part of this field, in Ohio, varies from 4–10 per cent; and that from the Indiana and Illinois field varies from 8–17 per cent.

The commercial value of a coal naturally decreases with the increase in the amount of moisture.

4. The ash of a coal is the incombustible residue left after all of the carbonaceous material has been burned. It consists of compounds of silica, alumina, calcium, magnesium, iron, and the alkali metals, and is derived from the original vegetable matter, or from the impurities formed during the formation of the coal bed.

The amount of ash in a coal influences its commercial value greatly, as the efficiency of combustion is influenced not only by the amount but also by the character of the ash. The fusibility of the ash is also an important factor, and there is a close relationship between the melting point of the ash and the tendency to clinker.

5. The volatile matter and fixed carbon represent respectively, the gaseous and solid material which are capable of being utilized by heating in a closed space. The former consists of carbon monoxide, hydrogen, methane and higher hydrocarbons, and the non-combustible gases, carbon dioxide and water vapor. The composition of the volatile matter varies greatly with the source of the coal, and the amount varies with the temperature of heating. The temperature of heating, 950°, is purely arbitrary and is a convenient one from the analyst's point of view. There is greater variation in results when heating at low temperatures than at the temperature selected. The fixed carbon and ash represent roughly the amount of coke which may be obtained from any coal.

6. Sulphur is present in coal as pyrite or marcasite, as sulphate of iron, aluminum or calcium, and as an organic compound. The presence of much pyrite increases the tendency of the ash to clinker, and thus decreases the commercial value of the coal. The sulphur present as an organic compound is without much influence except that it lowers the heating value.

7. Eschka's mixture is especially valuable in the oxidation of sulphur in coal, as more energetic oxidizing mixtures would oxidize the carbon with explosive violence. Oxidation of sulphur in coal by this method is a rather slow process, but a large number of determinations can be carried on simultaneously without much attention.

The Eschka mixture may also be applied to the oxidation of sulphur in mineral sulphides and to the determination of sulphur in iron and steel.

ANALYSIS OF PHOSPHOR-BRONZE

DETERMINATION OF TIN

Treat 0.5 gram of the borings in a No. 1 beaker with 15 cc. HNO_3 (sp. gr. 1.20). Evaporate the solution on the water bath or steam table until the residue is *just dry*, and remove from the heat as soon as this stage is reached. Prolonged heating of this residue must be avoided. Treat the residue with a mixture of 10 cc. HNO_3 (sp. gr. 1.42) and 50 cc. water, dividing the acid into three portions and boiling and decanting after each

addition through a 9 cm. hardened filter paper; finally complete the washing by *boiling* and decanting with distilled water until the metastannic acid is apparently free from copper. The first portion of filtrate should be carefully examined for metastannic acid, refiltered if necessary, and each successive clear filtrate should be removed from below the funnel before more wash water is added, as the precipitate is likely to run through the filter. Preserve the filtrate and washings for the determination of lead and copper. Leave as much of the metastannic acid as possible in the beaker during the washing. When the washing is completed and the filter has drained, remove the filter from the funnel, spread it out upon a watch glass, hold it vertically above the beaker containing the residue, and wash off all the visible residue into the beaker, limiting the amount of water as far as practicable. To dissolve the small amount of tin remaining in the filter, spread on the bottom of a beaker and pour over it 25 cc. of yellow ammonium sulphide solution and warm gently (covered) for 15 minutes. Meanwhile add 75 cc. of the sulphide solution to the metastannic acid in the beaker. Pour into this the sulphide from the filter and wash the filter three times with hot water. If the filter is perfectly white after washing out the sulphide, it may be discarded; otherwise it should be preserved and treated as directed below. Cover the beaker containing the sulphide solution and digest the solution on the steam table at a low heat for about two hours with occasional stirring. Filter off the copper and lead sulphides, receiving the filtrate in a 600 cc. beaker and wash with 100 cc. of dilute ammonium sulphide (1 volume ammonium monosulphide and 4 volumes of water). Complete the washing with water.

Treat the filter with 15 cc. of *hot* HNO_3 (1 part HNO_3 sp. gr. 1.42 to 4 parts water) passing it through the filter until the sulphides are dissolved. If the filter treated with ammonium sulphide was preserved, pass the same hot nitric acid solution through that filter and wash both filters completely, adding the filtrates and washings after neutralization with ammonia

to the copper and lead solution. Smoke off the filters in a weighed porcelain crucible and ignite finally at a high temperature, weighing the residue as SnO_2. This weight is to be added to that obtained below.

Dilute the ammonium sulphide solution to 500 cc., make distinctly acid with dilute acetic acid, but avoid a large excess. Cover the beaker and allow it to stand in a warm place for three to four hours, or over night. Decant the liquid through a filter, pour over the precipitate 150 cc. water, again decant and pour over it 150 cc. of dilute ammonium nitrate solution (2 gms. per 100 cc. H_2O acidified with a few drops of acetic acid). Again decant and transfer the precipitate to the filter, completing the washing with the nitrate solution. Transfer the moist filter and precipitate to a weighed porcelain crucible. Dry and smoke off the filter over a low flame, then gradually raise the temperature until the filter burns and the sulphur takes fire. Continue the gentle heating until there is no odor of sulphur dioxide, and then increase the heat gradually until the highest heat of the Tirrill is reached. A short heating over the blast lamp is advisable before final weighing. Ignite to constant weight. Weigh as SnO_2 and report as metallic tin.

Notes. — 1. The phosphor bronzes are essentially alloys of copper, tin, and phosphorus, but they may also contain lead and traces of other elements. They are characterized by their excellent qualities as a mechanical constructive material, the small effect which rise of temperature has upon the physical properties, and their desirable properties for bearings for high speed machinery and fairly heavy loads. For bearings they possess a low coefficient of friction and are hard enough to resist abrasion. They may be classified according to their mechanical properties into two groups: (1) the malleable phosphor bronzes; and (2) the cast phosphor bronzes.

The malleable phosphor bronzes are those in which the quantities of tin and phosphorus are relatively small, the upper limits of which may be taken as 6 per cent of tin and 0.3 per cent of phosphorus. The malleability is due to the fact that, with small amounts of phosphorus, copper phosphide, Cu_3P,

forms a homogeneous solid solution, and, further, with larger amounts of phosphorus, the tin promotes the separation of finely divided and widely disseminated copper-copper phosphide eutectic. Such alloys are useful for wire, gear wheels, pinions, bushings, worm wheel rims, etc.

The cast phosphor bronzes are particularly suited for bearings. The composition of such alloys varies widely, but the upper limits of tin and phosphorus may be placed respectively at 12 and 1.5 per cent. Lead is also a common constituent of these bearing metals and may be found sometimes to the extent of 10 per cent. These alloys show on microscopic examination the essential structure of a good bearing metal, viz.: a hard crystalline constituent embedded in a softer plastic matrix. The load is carried by the harder material while the plastic material provides for continuous lubrication. The presence of lead increases the amount of plastic substance.

2. In addition to the elements copper, tin, phosphorus and lead, bronzes may also contain antimony, arsenic, iron, aluminum, but, inasmuch as most of the commercial bronzes contain these elements only in traces, a special method has not been given for their separation. If it is found that antimony is present and it is desired to separate and determine it, reference should be made for details to Treadwell-Hall, Quantitative Analysis, 3rd Edition, p. 248. The principle of the separation is based on the insolubility of antimony sulphide in oxalic acid solution while stannic salts are not precipitated. Copper and lead are also held in small amounts in the residue and are left as sulphides after treatment of the antimony sulphide with ammonium polysulphide.

3. Evaporation to hard dryness of the metastannic acid causes it to lose water, and results in making it quite insoluble in ammonium polysulphide, and consequently considerable care should be exercised at this point. It is not even necessary to evaporate to complete dryness, as the subsequent boiling with dilute nitric acid will cause the complete separation of the metastannic acid.

4. Metastannic acid is not only finely divided and will pass through the finest filter paper, but it also has a strong tendency to become colloidal. Boiling the residue with separate portions of dilute nitric acid retards the formation of

the colloid and also removes small amounts of copper and lead, which are carried down with it.[1]

5. Stannic sulphide is thrown out of its sulpho-stannate solution with acetic acid, rather than with hydrochloric or sulphuric acids, because of its being a weaker acid. There is, therefore, less danger of re-dissolving the sulphide with a slight excess of acid.

As stannic sulphide is slightly soluble in solutions containing hydrogen sulphide in excess, it is essential to allow it to stand in a warm place until all hydrogen sulphide is removed. If this precaution is neglected, tin will appear in the filtrate. It is always advisable to test this filtrate for tin, passing hydrogen sulphide into the boiling solution.

6. The stannic sulphide, if washed with water, becomes colloidal on the removal of the electrolytes present and passes through the filter. It is therefore necessary to wash with an electrolyte to prevent this. Ammonium nitrate is chosen because it leaves no residue on ignition, and, further, it helps appreciably in burning the filter paper.

7. It is essential to heat the stannic sulphide at a low temperature at first because of the volatility of the sulphide. The burning of the sulphur furnishes enough heat. As soon as the sulphur is burned off the temperature may be raised without danger. Like silica and titanic oxide, stannic oxide loses its last traces of moisture only at the temperature of the blast. The color of this ignited oxide darkens slowly at the higher temperatures and usually varies in color from a light to a dark gray.

It is advisable in the ignition of any sulphide to oxide to heat with dry ammonium carbonate to remove traces of sulphate which might have formed during the ignition.

DETERMINATION OF COPPER AND LEAD

The filtrate from the metastannic acid should not exceed in volume 200–250 cc. To determine these two elements the solution is subjected to electrolysis until both have been completely precipitated, the copper as metal on the cathode, the

[1] This and other colloids may be conveniently coagulated by stirring into the solution some white of egg, which on heating will coagulate and bring down with it the substance which it is desired to filter.

lead as hydrated peroxide on the anode. For this purpose, clean two platinum electrodes, preferably of gauze, by immersing for some time in hot dilute nitric acid, washing with water and then with alcohol. Dry at 130° and weigh. Place the electrodes in the solution making the smaller the cathode, the larger the anode and begin the electrolysis with a current of 0.25 ampere. Continue this strength current from 4–6 hours,[1] and then reduce to 0.1 ampere. After 18–20 hours the electrolysis should be complete. The level of the liquid in the beaker should be raised by about one-eighth of an inch by the addition of water. After half an hour an observation should be made to see whether any more copper has been precipitated on the clean surface of the wire of the electrode. If the copper has been completely deposited, the wire of the cathode will remain perfectly bright just under the surface of the liquid. If any copper shows, this process must be repeated until it has all been removed from solution. When complete the solution should be siphoned off and the electrodes carefully washed with distilled water, the current being allowed to pass through the solution during the process of washing. Before disconnecting the electrodes insert a wire between the binding posts so as not to cut out any other solutions in the same circuit. Immerse the copper electrode in water, wash with alcohol, dry at 100°. Dry the lead peroxide after washing in water at 180° C.

The lead peroxide does not adhere as firmly to the electrode as the copper. A better deposit may be obtained by increasing the surface area of the electrode, and by having a matt surface. If any peroxide should become detached, the solution is decanted away from it, it is washed with water, and then by means of alcohol washed on to a weighed watch glass and the excess of alcohol is evaporated off. In this way small quantities of lead peroxide can be conveniently collected and weighed.

[1] If gauze electrodes are available the current may be increased to 4–5 amperes so as to bring down the copper and lead dioxide very much more rapidly, finishing the electrolysis in the course of several hours.

Notes. — 1. In nitric acid solution of copper and lead salts, the former is deposited on the cathode as strongly adhering metallic copper, and the latter on the anode as hydrated lead dioxide. Various views have been expressed to account for the deposition of lead as peroxide on the anode, and it is not certain whether lead nitrate hydrolyzes, giving rise to PbO_2^- ion, or whether a similar ion is formed from the decomposition of $Pb(NO_3)_4$.

2. Lead may be accurately separated from copper by taking advantage of the insolubility of lead sulphate in dilute sulphuric acid, but the simultaneous separation of the metals electrolytically produces results just as accurate, and for commercial work very much more convenient. The separation must take place in nitric acid solution and with a concentration of from 5 to 10 per cent by volume of the strong acid. This separation is not applicable in presence of metastannic acid, as both copper and lead dioxide are contaminated with it.

3. The time for electrolysis seems excessive, but where a large number of determinations are to be carried out from day to day this is not an important factor. Increasing the current density is out of the question because of the spongy, nonadherent deposits. Stirring the solution helps some, but the most efficient aid to rapid electrolysis is in the use of the rotating cathode or anode. By this process the solution is not only stirred, thus constantly bringing fresh solution to the electrode, but it is possible to obtain adherent deposits with high current density. The rotating cathode was proposed by Gooch and Medway,[1] and the rotating anode by Exner.[2] In each case the electrode was rotated at high speed by means of a small motor. Frary[3] proposed in place of the motor to place the solution in a solenoid and thus cause a rotation of the solution itself. Winkler[4] proposed the use of platinum gauze electrodes, but the advantages were not recognized until Stoddard had called attention to their use, and showed that there is economy of platinum and time, as well as avoidance of

[1] *Am. J. Sci.* (4), **15,** 320.
[2] *J. Am. Chem. Soc.,* **25,** 896.
[3] *Zeit. Electrochem,* 1907, 308.
[4] *Ber.,* **32,** 2192.

the more complicated apparatus. Stoddard[1] has obtained excellent results by using a gauze cathode. He operated at higher temperatures and used heavier currents than would be possible with plate electrodes, and reduced the time of operation to the limit of the rotating apparatus.

4. Washing, drying and weighing of the deposited copper must be carried out without unnecessary delay, in order to prevent oxidation. By careful ignition lead dioxide may be quantitatively converted into lead monoxide.

DETERMINATION OF PHOSPHORUS[2] IN PHOSPHOR-BRONZE

Weigh one gram of the borings into a No. 2 beaker and dissolve in 20 cc. of aqua regia, made by mixing just previous to use equal volumes of the concentrated acids. Have the beaker covered with a watch glass, and after solution is complete heat nearly to the boiling point of the solution for fifteen minutes. After cooling add 25 cc. of water, and then just sufficient ammonia (sp. gr. 0.90) to re-dissolve all of the copper hydroxide and to produce a deep blue colored solution. Now add 50 cc. colorless ammonium sulphide. This should be enough to precipitate the sulphides, and the supernatant liquid should show no blue color. If it does, more ammonium sulphide should be added. Digest at a temperature near the boiling point of the solution for fifteen minutes. Allow the precipitated sulphides of copper and lead to settle, filter into a 300 cc. Erlenmeyer flask, decanting the clear liquid carefully from the precipitate, and finally throwing the precipitate upon the filter. When the filter has drained put the filter and precipitate back into the beaker, add 50 cc. of ammonium sulphide wash water (one part colorless ammonium sulphide to three parts water) warm and stir occasionally for ten minutes; then pour the whole upon another filter, wash with 50 cc. of ammonium sulphide wash water and allow it to drain completely. The total volume should not be over 250 cc., but it is not necessary to evaporate in case this volume is

[1] *J. Am. Chem. Soc.*, **31**, 385.
[2] Dudley and Pease, *Eng. and R. R. Journ.*, March, 1894.

slightly exceeded. Add to the filtrate 10 cc. of magnesia mixture and shake. Place the flask in ice water and allow to stand with occasional shaking for two hours. Filter off the precipitate of magnesium ammonium phosphate upon a small filter and wash with ammonia water (one part 0.96 sp. gr. ammonia to three parts water) until nearly free from sulphide. Pour 10 cc. hydrochloric acid (one part HCl sp. gr. 1.20 to four parts water) into the flask, taking care that all of the precipitate adhering to the walls of the flask is dissolved, and then pour the acid through the filter, allowing the solution to run into a No. 1 beaker. Wash the flask and filter with 10 cc. more of the same acid. Add 3 cc. of magnesia mixture to the filtrate, and then add ammonia slowly with constant stirring until present in slight excess. Add 10 cc. ammonia sp. gr. 0.90, allow to stand in ice water for two hours, stirring the solution occasionally. Filter, and wash the precipitate with ammonia water until free from chlorides, and ignite with the usual precautions, weighing as $Mg_2P_2O_7$.

Notes. — 1. The principle of this determination is dependent upon the oxidation of phosphorus, existing in the alloy as phosphide, by means of aqua regia; separation of lead and copper as sulphides by means of ammonium sulphide, and after filtration the precipitation of magnesium ammonium phosphate in presence of ammonium sulpho-stannate.

2. Complete oxidation of the phosphorus cannot be accomplished by means of nitric acid alone, although many of the published methods are based on the quantitative separation of phosphorus along with the tin in the residue obtained after treatment with nitric acid. This process leads to erroneous results, as some of the phosphorus always remains unoxidized. Treatment with aqua regia seems necessary for complete oxidation.

3. Ammonia is added previous to the addition of ammonium sulphide so as to eliminate any unnecessary separation of sulphur. It forms with copper the complex ion $Cu(NH_3)_4^{++}$. Lead hydroxide remains undissolved in the ammonia, but is converted into sulphide by ammonium sulphide.

4. If the first precipitate of magnesium ammonium phos-

phate be allowed to stand too long, small amounts of metallic sulphides will precipitate with it. Shaking and standing in ice water promotes the separation of magnesium ammonium phosphate and lessens the danger of carrying down sulphides. The second precipitation is made to separate from traces of sulphides and so that the conditions of precipitation may be improved. See note 12, page 27. The ignition of this precipitate must be made with caution.

DETERMINATION OF CARBON IN STEEL

APPARATUS

The apparatus necessary for the direct combustion of carbon consists of an electrically heated furnace with suitable rheostat, an ammeter, a quartz combustion tube, a purifying train, an absorbing train, and a cylinder of compressed oxygen.

The furnace is preferably of the resistance type made by winding an alundum or clay tube with a resistance wire such as nichrome and surrounding the tube with insulating material to prevent loss of heat. The length of the furnace should be approximately 8 to 12 inches and it should have an opening capable of taking a quartz tube about $1\frac{1}{2}$ inches in diameter. Suitable furnaces can be made at low cost and several types may be obtained on the market at reasonable cost. A temperature of 1000° C. must be obtained without danger of burning out, and must be maintained for a long period of time. A suitable furnace running on a 110 volt-circuit at $3\frac{1}{2}$ to 4 amperes should give this temperature. Before placing the furnace in commission, and at intervals of two or three weeks it should be calibrated with a standard thermocouple, so that the operator may know the approximate temperature by the ammeter readings. By regulation of the rheostat, temperatures may be obtained and maintained within 5 to 10 degrees of that desired.

The quartz combustion tube should be about 24 inches in length and 1 inch in diameter. It should be glazed on the inner surface. Within the tube should be placed at a position corresponding to the front end of the furnace a two-inch roll

of ignited asbestos wrapped in nichrome gauze. This should be left permanently in place. A similar roll should be inserted in the rear of the tube after the introduction of the boat containing the sample. These rolls serve the purpose of protecting the rubber stoppers from the radiated heat.

In the center of the tube should be kept a cylinder of nickel foil slightly longer than the combustion boat to be used. This serves the purpose of protecting the walls of the quartz tube from oxide of iron formed during combustion.

The purifying train consists of a 12-inch porcelain tube $\frac{3}{4}$ inches in diameter containing granulated copper oxide, and a furnace capable of heating the tube to a dull red for 4 to 6 inches of its length. Attached to this tube is a tower containing fresh soda-lime and this in turn is connected with the rear end of the combustion tube.

At the front end of the combustion tube there is connected a bubble-tube containing granulated zinc and attached to this is a U-tube containing granulated calcium chloride, and beyond this is a Liebig potash bulb with its attached calcium chloride tube.

The apparatus is shown in Fig. 1. It is almost unnecessary to say that the apparatus should be tested to see that it is perfectly tight, and that before using it a blank should be run exactly as in the determination itself.

METHOD

Weigh 2–3 grams of finely divided sample, and distribute it evenly over the surface of a clay or alundum boat about half filled with RR. Alundum. Attach a potash bulb which has previously been weighed with oxygen in it from the blank determination. Place the boat containing the sample within the nickel cylinder in the centre of the heated tube, replace the asbestos plug, connect with the oxygen supply and adjust the rheostat so that the temperature will rise rapidly to 950–1000°. Regulate the flow of oxygen so that about 2–3 bubbles per second pass through the potash bulb. When combustion begins absorption of carbon dioxide will take place and the

rate of bubbling will diminish. Increase the flow of oxygen slightly during the next one or two minutes. After combustion is complete the rate of flow will be suddenly accelerated, and the flow should be regulated to 2-3 bubbles per second. Continue the passage of oxygen for 5-10 minutes. Disconnect the potash bulb, stop the supply of oxygen, and place the bulb in the balance. The increase in weight represents the carbon dioxide.
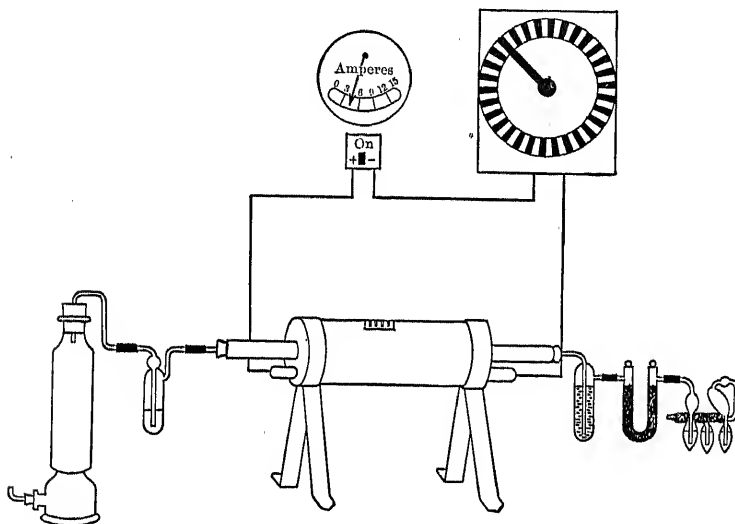
FIG. 1

DETERMINATION OF GRAPHITE IN CAST IRON

Dissolve 1 gram of sample in 35 cc. of nitric acid (sp. gr. 1.13), boil the solution from 5-10 minutes. Filter the residue on ignited asbestos in a small carbon funnel, wash several times with hot dilute potassium hydroxide solution (sp. gr. 1.10), followed by dilute hydrochloric acid, and finally with hot water. Dry at 100° C., transfer asbestos and graphite to a boat and burn as in the determination of total carbon.

Notes. — 1. Carbon exists in irons (> 1.70 per cent C.) and steels (< 1.70 per cent C.) in four forms; Iron Carbide, known as Cementite; Hardening Carbon; Graphite; Graphitic Temper Carbon.

Iron and carbon unite to form a carbide, Fe_3C, which is capable of being held in solid solution (austenite) the limiting value of which is 1.70 per cent carbon. It occurs in all slowly cooled (annealed) carbon steels, and in irons which have been chilled in passing from the liquid to the solid state. In hypo-eutectoid (< 0.85 per cent C.) steels, its formation takes place on passing slowly through the critical temperature, Ar_1, at 680°. At this temperature austenite decomposes into α iron and cementite, after having previously thrown out some of its iron (ferrite) at the critical temperature, Ar_3, which is progressively lowered with increase of carbon.

In hyper-eutectoid (> 0.85 per cent C.) steels the initial temperature of transformation of austenite into cementite rises with increasing carbon and reaches a maximum at 1.70 per cent carbon when cementite separates at 1130°. The ending of the transformation takes place at the same temperature for all compositions (0.85–1.70 per cent C.) at the Ar_1 point.

In eutectoid steels (0.85 per cent C.) complete transformation of austenite takes place at Ar_1 into an intimate mixture of its two constituents, iron (ferrite) and cementite, this mixture being known as pearlite. Thus hypo-eutectoid steels contain excess ferrite with pearlite, and hyper-eutectoid steels excess cementite and pearlite.

In irons of hypo-eutectic composition (1.70–4.30 per cent C.) cementite separates at 1130° as part of the eutectic of austenite and cementite, the austenite subsequently transforms at Ar_1 into pearlite. In hyper-eutectic (> 4.3 per cent C.) irons the initial separation of cementite rises progressively with increase of carbon and the final separation takes place at 1130°.

These facts are shown in the iron carbon equilibrium diagram, Fig. 2.

On slow cooling of *irons*, however, the above conditions are not realized, as the separated iron carbide almost immediately decomposes into graphite,

$$Fe_3C \rightarrow C \text{ (graphite)} + 3Fe$$
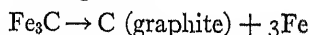
and the more slowly cooled the metal, the more complete is this reaction.

Dissolved in dilute hydrochloric or sulphuric acids, steels containing iron carbide evolve hydrocarbons. In dilute cold

nitric acid iron carbide separates as a brown flocculent residue which goes into solution above 80° and gives a color proportional to the amount which is present (Colorimetric Method).

The elements manganese, sulphur and chromium favor carbide formation, and silicon, phosphorus, and aluminum oppose it and promote graphite formation. Double carbides are formed with manganese, chromium, tungsten, molybdenum and vanadium.
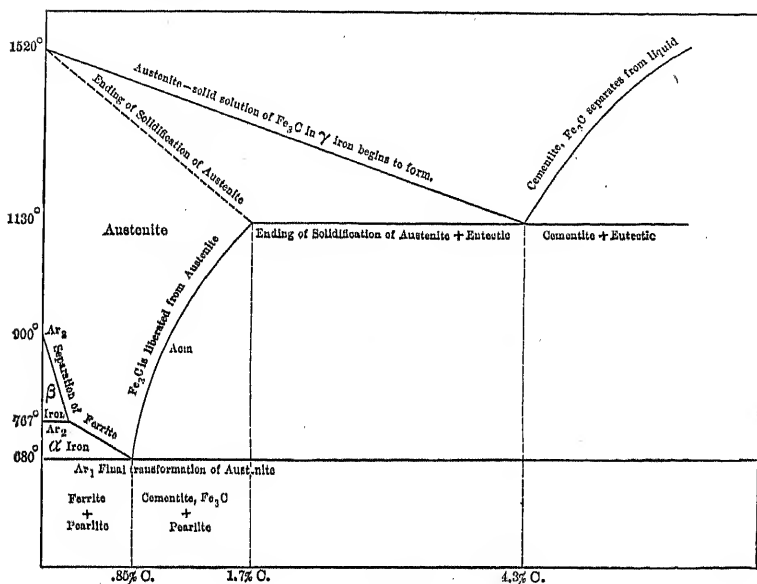

FIG. 2

The effect of carbide carbon upon the physical properties of steel is shown diagrammatically in Fig. 3.[1]

Hardening carbon is formed when a steel or iron is quenched from any temperature at which austenite exists, i.e., from above Ac_1. It is unstable and tends to pass back slowly on tempering (heating below Ac_1), and goes over completely to carbide carbon by heating above Ac_1 and cooling slowly.

It is decomposed by hot dilute acids. In dilute, cold nitric acid it at first separates as an insoluble residue and then goes into solution on shaking. The solution is colored in proportion to the amount of hardening carbon present.

[1] J. H. Nead, *Am. Inst. Min. Eng.* (1916), 2341.

Graphitic temper carbon is produced by heating irons rich
in cementite which decomposes at about 1000° into iron and

EFFECT OF CARBON ON PHYSICAL PROPERTIES
Heat Treatment—Annealed just above Ae₃.

A — Tensile Strength
B — Elastic Limit   Yield Point
C — Elongation
D — Contraction of Area
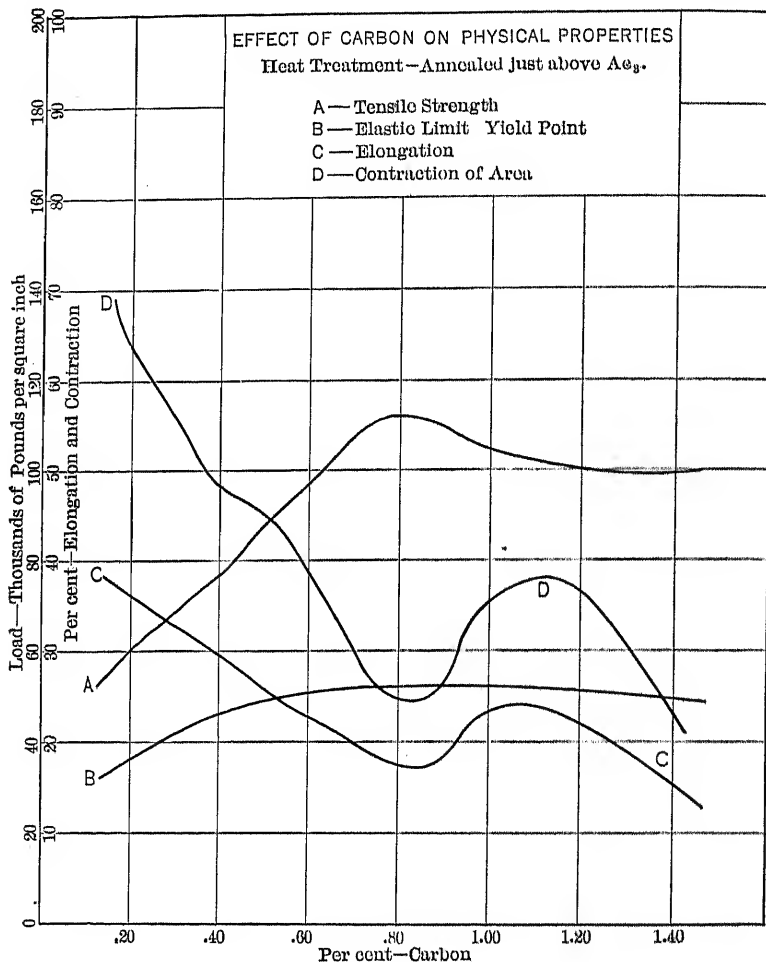
FIG. 3

graphitic temper carbon (Malleabilizing Process), and it is
sometimes formed in annealing high carbon steels.

Both graphite and graphitic temper carbon are unaffected
by boiling dilute acids. Boiling concentrated nitric acid
oxidizes them only very slowly. In oxygen, the amorphous

graphitic temper carbon is burned more readily than the crystalline graphite.

2. The carbon in plain carbon steels is completely burned at a temperature of 950–1000° C. In some alloy steels — chrome-nickel, chrome-tungsten, chrome-vanadium — complete combustion does not take place below 1050–1100° C., and on this account a flux is sometimes used, but it is preferable to burn direct if the temperature can be obtained.

3. Instead of using potassium hydroxide as absorbent, some workers prefer soda-lime, or barium hydroxide. If the latter is used the determination may be finished volumetrically by (1) filtering the precipitated barium carbonate and titrating the excess barium hydroxide, or (2) by dissolving the filtered barium carbonate [1] in excess standard acid and titrating for the excess.

4. The whole apparatus should be tested to see that there is no leakage of gas before proceeding with any determination. After having assembled the apparatus, and having been assured of its being tight, a blank determination should be made exactly as in the regular determination. The increase in weight of the potash bulb should not amount to more than 3 milligrams.

5. There is always difficulty in weighing accurately any piece of glass having a large surface area on account of the variations in the amount of condensed moisture. On this account it is always necessary to verify the weight of the potash bulb before beginning a day's work, and it is never allowable to assume the last weight of the day before. The bulb should always be wiped with a clean, dry cloth after handling and before being placed in the balance case.

Some of the soda-lime bulbs have small surface area and have a very considerable advantage in this respect over the potash bulbs.

DETERMINATION OF MANGANESE IN STEEL

VOLHARD METHOD

Standardization of Potassium Permanganate Solution. — Standardize the potassium permanganate solution in the follow-

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[1] Cain, *J. Ind. Eng. Chem.*, **6,** 465.

ing manner. From a burette measure into a 500 cc. Florence flask several portions of about 25 cc. each of a manganous chloride solution,[1] the value of which has been very accurately established according to the method given on page 17. Add 20 cc. zinc nitrate solution (300 grams $Zn(NO_3)_2,6H_2O$ per liter), dilute with hot water to about 300 cc., add two or three drops of dilute nitric acid, and heat to near the boiling point. Now add rapidly nearly as much permanganate solution as it is thought will precipitate all of the manganese. Rotate the solution thoroughly; and then add, cautiously, enough permanganate solution to give a permanent color to the supernatant liquid.

METHOD

For steels containing about one per cent of manganese weigh a three-gram sample; for higher percentages of manganese use a correspondingly lower weight. Place the borings in a porcelain casserole and treat with 30 cc. of nitric acid (sp. gr. 1.20). When solution of the metal is complete raise the watch glass by supporting it on a glass triangle, and evaporate to dryness. Then remove the watch glass and carefully bake the contents of the dish until no more oxides of nitrogen are evolved. After the casserole has cooled, add 20 cc. concentrated hydrochloric acid and heat until all ferric oxide is converted into chloride. (If cast iron is being analyzed, the solution should be evaporated to dryness, taken up in hydrochloric acid, and the graphite and dehydrated silica filtered off.) Concentrate the solution to remove the excess acid and transfer it to a 500 cc. calibrated flask, and dilute to about 200 cc. Now add, cautiously, strong sodium carbonate solution a little at a time until the precipitate just redissolves and the solution becomes colored deep red.[2] Then add slowly in small amounts zinc oxide suspended in water, shaking the flask after each addition, and continue this process until a point is reached where the ferric hydroxide

[1] Six grams of the crystallized salt dissolved in one liter of water.
[2] Compare Spathic Iron Ore Procedure.

suddenly coagulates. Allow the precipitate to settle, and fill the flask with water exactly to the graduation mark. Mix the contents of the flask thoroughly by pouring back and forth into a *dry* beaker several times. Allow the mixture to settle, and then filter through a four-inch *dry* filter paper. Collect 250 cc. of the filtrate, after the rejection of the first five cubic centimeters, in a graduated flask. Transfer this solution to a 500 cc. Florence flask, add two drops of dilute nitric acid, heat to near the boiling point, and titrate with potassium permanganate to pink color, exactly as in the standardization.

Notes. — 1. Manganese exists in ordinary steels in the form of a solid solution with iron. Small amounts are also present in the forms of manganese sulphide, MnS,[1] and manganese silicate, $Mn_2Si_3O_8$,[2] which form part of the slag found in steels. In manganese steels, ferro-manganese and spiegeleisen there is, in addition to the solid solution, some manganese as carbide, Mn_3C_2, or as a double manganese-iron carbide. Manganese is primarily put in steel for the purpose of deoxidizing and desulphurizing the melt, so as to prevent "red shortness" or brittleness during the forging heats. Some excess always appears in the finished product, and in commercial steels is found in amounts varying from 0.2 to about 1.00 per cent. In such amounts it increases the strength and hardness and decreases somewhat the ductility. These effects are more pronounced in high carbon steels than in low carbon material.

In metals containing manganese in excess of 1 per cent the hardness and brittleness increase rapidly and reach a maximum between 5 and 6 per cent. In such products the hardness and brittleness are so great that it is impossible to machine them with any tool. Beyond 7 per cent of manganese there is a progressive increase in the ductility, and steels containing about 13 per cent manganese are characterized by great strength, toughness and high ductility. Such steels are known as manganese steels and have found extensive application in the industries.

Manganese lowers the critical temperature, Ar_1. With in-

[1] Osmond and Werth, *Annales des Mines*, 1885.
[2] Stead, *Iron and Steel Magazine*, 9, 105.

creasing percentages of manganese the critical temperature finally falls below the ordinary room temperature, and self-hardening steels result. See notes on Carbon, page 61.

2. The principle of the Volhard method is based upon the reaction

$$2KMnO_4 + 3MnSO_4 + 2H_2O = 5MnO_2 + 2KHSO_4 + H_2SO_4.$$

That is, when potassium permanganate is added to a neutral manganous salt, all of the manganese in the latter is oxidized to the dioxide and the permanganate is reduced to the dioxide.

The reaction never takes place exactly as represented in the equation, except in the presence of a few drops of nitric acid and the salt of some heavy metal. In the absence of these substances the manganese is not oxidized completely to MnO_2. This is provided for in the standardization by the addition of zinc nitrate solution, and in the determination by the reaction of the ferric sulphate with the zinc oxide.

$$Fe_2(SO_4)_3 + 3ZnO + 3H_2O = 2Fe(OH)_3 + 3ZnSO_4.$$
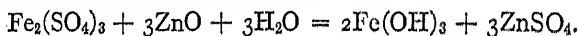
3. Since two molecules of potassium permanganate will oxidize three atoms of manganese, and since, in acid solutions, the same amount of permanganate will oxidize ten atoms of iron, it follows that 10Fe is equivalent to 3Mn. Having established the value of the permanganate solution in terms of iron or sodium oxalate, it would be a simple matter to calculate its value in terms of manganese. This calculation should be made so as to check the value obtained by titrating against manganous sulphate, but the latter value should be used on account of its having been obtained under exactly the same conditions as in the actual determination. The difference between the two values is usually extremely small.

4. In the standardization, and also in the actual titration, it is impossible to add an excess of potassium permanganate and then to titrate back with manganous sulphate solution, on account of the fact that manganese dioxide reacts catalytically with permanganic acid,[1] which liberates oxygen according to the following equation:

$$2HMnO_4 = H_2O + 2MnO_2 + 3O,$$
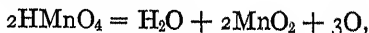
thus losing three-tenths of the oxygen which should have been used in oxidizing manganese sulphate.

[1] Morse, Hopkins and Walker, *Am. Chem. J.*, **18**, 401.

5. The Volhard method is particularly well adapted for the determination of manganese in those products where the manganese content is high, i.e., above 1 per cent. With lower content than 0.50 per cent there is difficulty in getting a satisfactory separation of manganese dioxide without unduly increasing the weight of sample.

The method is not applicable to the analysis of chrome steels as the zinc oxide may precipitate chromium only incompletely, in which case it might be oxidized by the potassium permanganate. Cobalt and vanadium interfere in a similar manner.

In steels rich in nickel it is difficult to obtain a satisfactory end point.

WILLIAMS METHOD [1]

Weigh two three-gram samples into 750 cc. Erlenmeyer flasks and cover with 100 cc. nitric acid (sp. gr. 1.42). Place the flask covered with a small watch glass on the steam table and allow it to remain until solution is complete. As the steel becomes *passive* on treatment with strong nitric acid, it is of little advantage to try to hurry the solution by boiling. When the steel is completely dissolved, add three grams of potassium chlorate, and after five minutes add a second portion of three grams, heating on the steam table during this time. After ten minutes remove from the steam table and heat for five minutes in a hood with


FIG. 4

good draught until the excess chlorine dioxide is driven off.
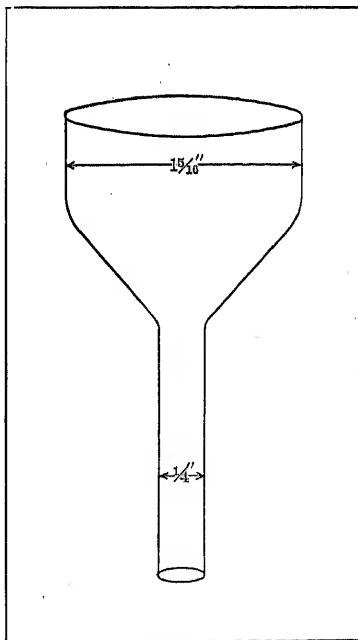
[1] *Trans. Am. Inst. Min. Eng.*, **10**, 100.

Cool, and filter without undue delay on asbestos which has
been previously treated with dilute hydrochloric acid and
washed with water until the asbestos does not reduce dilute
potassium permanganate solution. The asbestos should be
placed on a platinum spiral, a few pieces of glass tubing, or
some glass beads in the bottom of a manganese funnel. When
the excess of nitric acid has drained off, place a clean beaker
under the funnel, begin to wash with water, and continue
until litmus paper shows no test for nitric acid. Then wash
the manganese dioxide and asbestos back into the flask in
which the precipitation was made.

Add 50 cc. ferrous sulphate solution (50 cc. H_2SO_4 sp. gr.
1.84; 5 grams $FeSO_4.7H_2O$; 450 cc. H_2O) the value of which,
in terms of potassium permanganate, has recently been es-
tablished. Dilute to 200 cc. with water. Shake until the
manganese dioxide has completely dissolved, and titrate to
pink color with potassium permanganate.

Notes. — 1. The principle of this method is based upon the
two reactions:

$$Mn(NO_3)_2 + 2HClO_3 = MnO_2 + 2ClO_2 + 2HNO_3.$$
$$MnO_2 + 2FeSO_4 + 2H_2SO_4 = MnSO_4 + Fe_2(SO_4)_3 + 2H_2O.$$
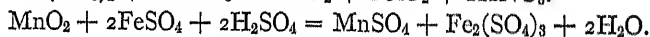
The oxidation of manganous nitrate to dioxide will take
place only in concentrated nitric acid solution. Dilute nitric
acid may be used to dissolve the steel, but, if used, the solution
must be concentrated before adding the potassium chlorate,
otherwise incomplete oxidation will result.

Since one molecule of manganese dioxide will oxidize two
molecules of ferrous sulphate it is evident that one manganese
is equivalent to two atoms of iron. This ratio is used in the
calculations, and the iron value of the potassium permanganate
is taken as the standard. The manganese value of the potas-
sium permanganate in the Williams method should be five-
thirds of the strength found in the Volhard method.

2. This method is well adapted to the determination of
manganese in steels containing not more than 0.75 per cent of
that element. With higher amounts the filtration of the
dioxide becomes more and more difficult unless the size of the

sample is correspondingly decreased, and, further, there is an increasing error with an increase in the amount of manganese dioxide precipitated. As the precipitate is not absolutely pure MnO_2, but contains slightly less oxygen than represented by the formula, it will be seen that the error increases with the amount of dioxide thrown out of solution.

As the precipitate loses oxygen slowly on standing, it is important to filter as soon as possible after precipitation.

The method is not especially well adapted to cast irons on account of the difficulties of filtration in the presence of graphite and gelatinous silica.

3. Care should be exercised in the addition of potassium chlorate. If added to a boiling solution dangerous explosions may result.

4. Some asbestos, either because of its containing ferrous iron or organic matter, reduces potassium permanganate. It is, therefore, necessary to test each new lot to see whether or not it will react with very dilute permanganate solution. This difficulty might be obviated by passing the reducing solution, ferrous sulphate, or oxalic acid, through the funnel containing the manganese dioxide, but it is much simpler to avoid the washing this would involve by putting the dioxide and asbestos into the reducing solution.

5. Almost any standard reducing solution may be used to react with manganese dioxide. Ferrous sulphate and oxalic acid are the most commonly used. Ferrous sulphate in acid solution is fairly stable and has the very distinct advantage of reacting in the cold. Oxalic acid reacts only when warmed and has the disadvantage of changing concentration, unless sterilized, because of organic growth in the solution.

Whatever the reducing solution used, a blank should be made before each day's work against the standard potassium permanganate.

6. It is impossible to ignite the precipitated dioxide and weigh as Mn_3O_4, because of the occluded iron and the indefiniteness of composition of the ignited oxide. Provision may be made for the separation of the iron, and the determination may be finished as given on page 17.

7. The method is applicable in the presence of all the constituents of the more common steels.

THE BISMUTHATE METHOD FOR MANGANESE

Weigh into a 250 cc. Erlenmeyer flask about one gram of borings and treat with 50 cc. of nitric acid (sp. gr. 1.13). Heat until solution is complete, allow to cool, and then add about 0.5 gram of sodium bismuthate. Rotate the contents of the flask, and heat until the pink color has disappeared. If the solution shows precipitated manganese dioxide, add crystals of ferrous sulphate, free from manganese, until it becomes clear. Heat for two minutes to remove oxides of nitrogen, and cool to about 15°. Now add 2 to 3 grams of sodium bismuthate, and agitate the contents of the flask for several minutes. Dilute with 50 cc. of three per cent nitric acid,[1] and filter through asbestos, as prescribed in the previous method, into a 300 cc. Erlenmeyer flask. Wash the asbestos with 50 to 100 cc. of cold three per cent nitric acid. Run into this solution 50 cc. of the ferrous sulphate solution which was used in the Williams method, and titrate back to pink color with standard potassium permanganate.

The value of the ferrous sulphate solution in terms of potassium permanganate must be determined in the following manner. Measure into a 250 cc. Erlenmeyer flask 50 cc. of cold nitric acid (sp. gr. 1.13), add about 0.5 gram of sodium bismuthate, agitate, and filter through asbestos. Dilute with 50 cc. of cold three per cent nitric acid, run in 50 cc. of ferrous sulphate solution, and titrate with permanganate solution to pink color.

Having determined the value of the permanganate solution in terms of ferrous sulphate, the manganese in the sample is represented by the difference between the amounts of permanganate solution actually used in the determination and in the titration of a volume of ferrous sulphate equivalent to that used in the determination.

Notes. — 1. The method originated with Schneider,[2] who used bismuth tetroxide as the oxidizing agent. This oxide is

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[1] 30 cc. of HNO_3 (sp. gr. 1.42) to one liter of water.
[2] *Dingler's Polytech. J.*, **269**, 224.

very difficult to prepare free from chlorides, and, as traces of hydrochloric acid interfere with the sharpness of the end point, it was abandoned by Reddrop and Ramage,[1] who proposed the use of sodium bismuthate. More recently the method has been studied and recommended by Blair[2] and by Blum.[3]

Sodium bismuthate is supposed to be the sodium salt of the hypothetical bismuthic acid, $HBiO_3$. The product sold under this name is probably of indefinite and variable composition.

2. The method is based upon the fact that sodium bismuthate oxidizes a manganous salt *in the cold* to permanganic acid, which can be reduced by ferrous sulphate the value of which is known in terms of standard potassium permanganate. Ferrous sulphate is not readily acted upon by cold nitric acid and can consequently be used to reduce the permanganic acid without introducing an error.

Lead peroxide oxidizes manganese to permanganic acid in hot solution, but the results are not reliable when more than two per cent of manganese is present. In hot solution permanganic acid oxidizes some of the manganous nitrate to dioxide.

3. Since two molecules of permanganic acid will give up five atoms of oxygen, it follows that it will oxidize ten atoms of iron.

Hence

$$2HMnO_4 = 10Fe,$$
$$1Mn = 5Fe.$$
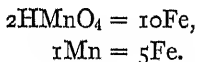
From these equations it can be seen that the value of the standard potassium permanganate may readily be obtained in terms of manganese from the iron standard.

The value may be determined directly in terms of manganese by using a definite volume of standard manganous sulphate solution. This solution may be oxidized and determined by the bismuthate process, exactly as described in the procedure.

4. The addition of a small amount of sodium bismuthate to the hot solution is to oxidize the hydrocarbons formed by the decomposition of iron carbide. The excess bismuthate is

[1] *J. Chem. Soc.*, **67,** 268.

[2] *J. Am. Chem. Soc.*, **26,** 33.

[3] *J. Am. Chem. Soc.*, **34,** 1379.

rapidly decomposed by the hot nitric acid, and then the latter reacts with the permanganic acid, precipitating manganese dioxide. This in turn is reduced by the addition of a small amount of ferrous sulphate.

5. It is stated that chromium in small amounts does not interfere with this method, but this is contrary to the author's experience. For accurate work it is necessary to remove iron and chromium with zinc oxide, and to oxidize an aliquot part of the filtrate with sodium bismuthate.

Tungsten steels, which decompose readily in nitric acid, may be heated to precipitate the tungstic acid, and, after filtration, may be carried through as ordinary steels. If solution of the steel is troublesome, it will be necessary to use aqua regia and to remove subsequently every trace of hydrochloric acid by repeated evaporation with nitric acid.

6. There must be no loss of time between the filtration and the addition of ferrous sulphate, as permanganic acid gradually decomposes on standing, and the warmer the solution is the more rapidly does decomposition take place.

7. The bismuthate method combines extreme accuracy with great rapidity and simplicity of manipulation. It is capable of being used, without loss of accuracy, for any percentage of manganese. In this respect it has a distinct advantage over the Volhard and Williams methods.

8. A colorimetric method, in which oxidation to permanganic acid is brought about by sodium bismuthate, ammonium persulphate, or lead peroxide, is extensively used for rapid work in the steel mills. The color of the permanganic acid formed is compared with that produced in steels of known manganese content.

9. A method, very similar in its details and principle, is in extensive use. Instead of using sodium bismuthate as oxidizing agent, ammonium persulphate[1] is used. While, in general, not so accurate, it possesses the distinct advantage that the excess reagent is destroyed by heat, thus avoiding one filtration.

10. All methods involving oxidation of manganese to permanganic acid are not applicable to cast irons, unless the separated carbon is filtered off before oxidation takes place.

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[1] Walters, *Proc. Eng. Soc.*, Western Penna., **17** (1901), 257; *Chem. News*, **84**, 239.

DETERMINATION OF PHOSPHORUS IN IRON AND STEEL

STANDARDIZATION OF POTASSIUM PERMANGANATE AND THE USE OF THE JONES REDUCTOR

Dissolve 5 grams of potassium permanganate in two liters of water, and filter this solution through some washed asbestos into a clean bottle. It is advisable to keep this solution in a cool place and protected from the light.

Weigh several portions of pure iron wire of about 0.20 gram each into 125 cc. Erlenmeyer flasks, and pour into each flask 30 cc. of water and 10 cc. of concentrated sulphuric acid. Cover with a watch glass and heat until solution is complete. Add enough strong permanganate solution, drop by drop, until the color of the permanganate disappears only slowly. If an excess be added, it is necessary to reduce by a drop of sulphurous acid and to boil off this excess completely.

Having previously gotten ready a Jones reductor, by washing with hot dilute sulphuric acid followed by hot water, attach the reductor to the filter pump, and, in *making blanks* or in *any determination*, proceed exactly as here described.

Pour 100 cc. of hot dilute sulphuric acid (made by adding 25 cc. of concentrated sulphuric acid to one liter of water) into the funnel, and open the stopcock. When only a little remains in the funnel add the solution to be reduced. This solution should also be hot. Have ready 250 cc. of hot, dilute sulphuric acid, and when the solution to be reduced has nearly passed out of the funnel wash out, with this acid, the beaker containing the iron or molybdenum solution, as the case may be, and pass the whole of the 250 cc. of acid through the reductor. Follow this by 100 cc. of hot water. Disconnect the flask and titrate with potassium permanganate solution.

Before any series of determinations, a blank must be made on the reductor. In this case a mixture of 10 cc. concentrated sulphuric acid, 5 cc. dilute ammonia, and 50 cc. of water is to be passed through the reductor, preceded and

followed by the dilute acid as described above. The amount of potassium permanganate used in this operation, which usually is about 0.3 cc., must be subtracted from the total amount taken in each determination. Having made a blank, this value will serve for a series of determinations, but a new blank should be made before each new series.

<div style="text-align:center">

METHOD

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For steels weigh 2 grams, and for irons weigh a 1 gram sample into a 250 cc. Erlenmeyer flask. Add 100 cc. of nitric acid (sp. gr. 1.13) which has been prepared by mixing one part of nitric acid (sp. gr. 1.42) with three parts of water, and which has been tested by means of a Westphal balance. Cover the flask with a small watch glass, and heat the solution until the oxides of nitrogen have boiled off. Then add 10 cc. of potassium permanganate solution (15 grams of the crystals to one liter of water), or, in the case of irons or steels rich in iron carbide, enough of the solution to produce a pink color. Boil until the pink color disappears and then remove from the heat. Now add at intervals crystals of ferrous sulphate free from phosphorus until all of the manganese dioxide is dissolved. Boil two minutes longer and then cool the flask. Add cautiously 40 cc. of dilute ammonia (sp. gr. 0.96) and rotate the flask until the precipitated ferric hydroxide is dissolved. When the solution has cooled to about $35°$ C. add 40 cc. of a recently filtered solution of ammonium molybdate,[1] close the flask with a solid rubber stopper, and shake for five minutes. Allow the precipitate to settle for a few minutes, and filter through a 9 cm. paper which fits the sides of the funnel perfectly. Wash the precipitate several times by decantation, and then completely on the filter with a solution of acid ammonium sulphate (made by adding 25 cc. of

[1] MOLYBDATE SOLUTION. — To 100 grams of pure molybdic oxide (MoO_3) which has been stirred up with 400 cc. of cold, distilled water add 80 cc. of concentrated ammonia. Filter, and pour the filtrate slowly, with constant stirring, into a solution of 400 cc. nitric acid (sp. gr. 1.42) in 600 cc. of water. After the addition of 50 milligrams of microcosmic salt, allow to stand for twenty-four hours, and filter.

strong sulphuric acid to 15 cc. of strong ammonia in one liter of water).

Test the wash water for molybdenum by allowing about ten drops to run into a small specimen tube containing *one* drop of yellow ammonium sulphide. Compare the color in this tube with a similar tube which has been treated with a like amount of acid wash water and a drop of the polysulphide. Continue the washing until all of the molybdenum is removed.

Now pour 5 cc. of ammonia (sp. gr. 0.90) and 20 cc. of water into the flask to dissolve any ammonium phosphomolybdate adhering to the walls; pass this solution through the filter and allow the filtrate to run into a No. 2 beaker. Wash out the flask and the filter with about 75 cc. of water. To this solution add 10 cc. of concentrated sulphuric acid and pass through the reductor exactly as previously described, taking the precaution not to allow any air to enter the reductor. This solution is preceded and followed by the dilute sulphuric acid and water, just as in testing the reductor. When the water has finally been drawn through with the exception of a small amount in the funnel, the flask is detached and the reduced solution is titrated at once with the standard potassium permanganate to a permanent pink color.

Subtract from the reading of the burette the blank for the reductor and calculate, assuming a reduction of the molybdenum to $Mo_{24}O_{37}$ by the zinc, and oxidation to MoO_3 by the permanganate.

THE FERRIC ALUM METHOD FOR PHOSPHORUS[1]

Proceed exactly as in the preceding method up to the point of passing the sulphuric acid solution through the reductor. Instead of passing the reduced solution into the empty flask, place in the flask 50 cc. of ferric alum solution,[2] and allow the reduced solution to run through a tube

[1] This method was worked out in the laboratory of the Penna. R.R. by Dudley and Pease but was never published by them. It has been in successful use in this laboratory for many years.

[2] 100 grams of $Fe_2(SO_4)_3(NH_4)_2SO_4.24H_2O$ dissolved in 1000 cc. H_2O, to which has been added 25 cc. H_2SO_4 (sp. gr. 1.84). To this solution add 40 cc. H_3PO_4.

extended below the surface of the liquid. In all other respects the two methods are identical. The purpose of the ferric alum is to oxidize immediately the molybdenum, which has been reduced in the reductor to a form corresponding to the oxide Mo_2O_3, to the higher oxide MoO_3. The iron which has been reduced in this reaction is then titrated with potassium permanganate solution, and is a direct measure of the molybdenum reduced. The calculation is based on the assumption that the molybdenum is reduced to Mo_2O_3, and the results should agree with the other method in which reduction to $Mo_{24}O_{37}$ was assumed.

A blank determination must be made with the ferric alum solution in the flask, using the same amounts of reagents as in the regular procedure.

Notes. — 1. The determination of phosphorus is an indirect method dependent upon its oxidation to phosphoric acid and precipitation in the form of ammonium phospho-molybdate, the reduction of the molybdenum by means of zinc, and the subsequent oxidation of the molybdenum by means of potassium permanganate.

2. The phosphorus exists in most steels as a solid solution of iron phosphide (Fe_3P) in iron. When present, as it may be in some irons, in amounts greater than 1.7 per cent it separates as free Fe_3P, and the iron will contain the solid solution, and also free iron phosphide. In wrought iron, and probably also in some low carbon Bessemer steels, phosphorus may also exist in the form of a phosphate.

3. The preparation of potassium permanganate which is to be used for a series of determinations should be done with extreme care. The crystals of the salt are never absolutely pure, but invariably contain a small amount of manganese dioxide. If this is not filtered off, it reacts with the potassium permanganate, giving off oxygen and forming more manganese dioxide. The presence of manganese dioxide accelerates the decomposition, and when it is once formed the decomposition takes place rapidly. A solution carefully prepared will keep almost indefinitely.

4. It is impossible to obtain absolutely pure iron wire. The determination of the actual amount of iron in any sample

may be done in either of two ways: the impurities in the sample or the actual amount of iron may be determined. The former method involves much skill and experience; the latter method is the simpler and is, perhaps, more accurate. When using the latter method, the potassium permanganate is titrated first against pure electrolytic iron,[1] and after this has been carefully standardized this solution is used to determine the actual amount of iron in a sample of pure piano wire.

There are many other methods for the standardization of potassium permanganate solutions. The author prefers the use of sodium oxalate to any of the others. This salt contains no water of crystallization, is very stable, may easily be prepared pure, and may also be used as a standard for alkalimetric work.[2]

5. The addition of strong potassium permanganate to the solution of iron is rendered necessary because of the presence of a small amount of carbon. The decomposition of iron carbide by sulphuric acid gives rise to hydrocarbons which are held in solution and which would affect the titration, if not previously oxidized.

6. A blank on the reductor is a necessity on account of the fact that all zinc contains some iron which is given up to the dilute acid passing through the column of zinc. The necessity, therefore, of always using exactly the same amounts of reagents is apparent. The time factor is also apparent. It is advisable to measure accurately all reagents, and in each case to allow approximately the same amount of time for each reaction.

7. The preparation of nitric acid of exact sp. gr. 1.13 is important because in acid of this strength the steel is most readily soluble, the phosphorus is oxidized as well as in acids of greater strength, the silica is not separated in the insoluble form, and it is very important to bring down the yellow precipitate always in the same strength solution. Especially on account of this last reason, the solutions should never be allowed to boil longer than the time indicated in the directions.

8. Boiling off the oxides of nitrogen seems to be necessary

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[1] For details in carrying out this method, consult Treadwell-Hall's Analytical Chemistry, Vol. II, p. 93.

[2] See Spathic Iron Ore Procedure, p. 21.

as these reduce potassium permanganate, which is to be added subsequently to this operation, and also on account of the solubility of the ammonium phospho-molybdate in solutions containing nitrous acid.

9. Potassium permanganate is added to complete the oxidation of the phosphorus to the form of ortho-phosphoric acid and to destroy the carbonaceous material. When carbide of iron is boiled with dilute nitric acid certain organic compounds are formed, which, if allowed to remain, would hold some of the yellow precipitate in solution.

For most steels 10 cc. of permanganate solution is more than enough to oxidize the phosphorus and destroy the carbonaceous material. It is advisable, however, to use just this amount in each case except in high carbon steels or in white irons, which may require more than the specified amount to complete the oxidation.

10. Instead of using pure ferrous sulphate for the removal of the manganese dioxide, many other substances, such as sulphurous acid, oxalic acid, sugar, sodium thiosulphate, etc., have been recommended, but it is believed that for student work ferrous sulphate is the most satisfactory.

11. The addition of ammonia is simply to form some ammonium nitrate in which the precipitate is more insoluble. If by some oversight too much nitric acid had been boiled off during the operation, the ammonia will produce a permanent precipitate of ferric hydroxide. If this should happen, it is necessary to add more nitric acid of sp. gr. 1.13.

12. The composition of ammonium phospho-molybdate depends very largely upon the strength of solutions from which it is precipitated and upon the temperature of precipitation. Produced under the conditions described above it may be represented by the formula $(NH_4)_3PO_4, 12MoO_3$. The ratio of phosphorus to molybdenum is always $P : 12MoO_3$. If precipitation takes place at a temperature higher than $35°-40°$ C., there is liability of ammonium arseno-molybdate being precipitated in case there is any arsenic in the sample.

All of the molybdenum before passing through the reductor is in a form corresponding to the oxide MoO_3, and is reduced in the reductor to a form corresponding to the oxide Mo_2O_3. It is, however, so sensitive to the action of

oxygen that on coming in contact with the air[1] in the flask it takes up oxygen from the air, and is oxidized to a form corresponding to the oxide $Mo_{24}O_{37}$.[2] The calculation of results must, therefore, be based upon this reduction.

13. Having standardized the potassium permanganate solution against iron, the conversion of the iron value to the phosphorus value is very simple, as is shown by the following equations:

$$2KMnO_4 \backsimeq 5O \backsimeq 10Fe.$$
$$Mo_{24}O_{37} + 35O = 24MoO_3.$$
$$2P \backsimeq 24MoO_3 \backsimeq 70Fe.$$
$$P \backsimeq 35Fe.$$
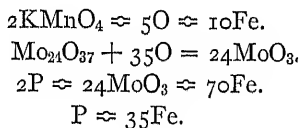
In the ferric alum modification advantage is taken of the fact that ferric iron will oxidize reduced molybdenum solutions. The molybdenum in the form of Mo_2O_3 as it leaves the reductor reduces a corresponding amount of iron to the ferrous condition, and is in turn oxidized to MoO_3. As the ferrous iron is more stable than reduced molybdenum solutions, the titration is on the whole more satisfactory.

14. As the ammonium phospho-molybdate has a strong tendency to crawl, it must be filtered through a paper which fits the funnel perfectly. Otherwise it creeps over the top of the paper and into the filtrate. It is necessary to wash the edges of the paper thoroughly, so as to remove the last traces of iron and molybdenum. If the iron is not removed it will color the drop of yellow ammonium sulphide black while it is still alkaline. The presence of molybdenum is shown by its coloring the precipitated sulphur brown. When free from molybdenum the sulphur will be perfectly white.

15. The determination of phosphorus in most of the alloy steels involves no special difficulties and the regular procedure is applicable except in the presence of large amounts of tungsten, vanadium, or chromium when special methods must be used. In steels containing chromium an insoluble residue, probably chromium carbide, is left on treating with nitric acid. This goes into solution slowly on digestion at a low temperature. It is advisable to keep the solution at constant volume by the occasional addition of some water.

[1] W. A. Noyes, *J. Am. Chem. Soc.*, **16**, 553.
[2] Blair and Whitfield, *J. Am. Chem. Soc.*, **17**, 747.

16. The best method for the gravimetric determination of phosphorus is the one which makes use of the basic acetate separation of the phosphoric acid along with some of the iron and the subsequent separation, after the addition of citric acid to hold the iron in solution, as magnesium ammonium phosphate.

ALKALIMETRIC METHOD FOR PHOSPHORUS

HANDY METHOD

Proceed exactly as in the preceding methods to the point of washing the ammonium phospho-molybdate precipitate. Instead of using acid ammonium sulphate solution, wash with 1 per cent nitric acid [1] to remove iron salts, and follow with 1 per cent potassium nitrate until litmus paper shows freedom from acid. Transfer the precipitate with the filter paper to the flask in which precipitation was made, cover with enough tenth-normal sodium hydroxide solution to completely dissolve the yellow precipitate, using a slight excess, and then titrate with tenth-normal nitric acid using phenolphthalein as indicator.

Notes. — 1. The reaction upon which this method is based is the following:

$$2(NH_4)_3PO_4.12MoO_3 + 46NaOH = 2(NH_4)_2HPO_4 \\ + (NH_4)_2MoO_4 + 23Na_2MoO_4 + 22H_2O.$$
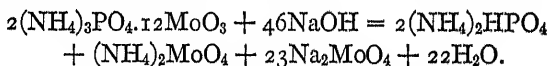
It is thus seen that the ratio of phosphorus to sodium hydroxide is, $P \backsim 23NaOH$, and upon this basis the calculations are made.

2. This method is extensively used, is more rapid than the methods involving reduction of the molybdic acid, and is accurate for the average steel.

3. Standardization of the sodium hydroxide solution is made preferably against the yellow precipitate obtained from a steel in which the phosphorus has been accurately determined by some other method. It is needless to say that the sodium hydroxide solution must be protected from carbon dioxide of the air and must be prepared free from carbonates

[1] Add 13 cc. nitric acid sp. gr. 1.42 to 1 liter of water.

by the introduction, at the time of solution, of a small volume of barium hydroxide solution.

DETERMINATION OF SULPHUR IN STEEL

EVOLUTION METHOD

Standardization of Iodine and Sodium Thiosulphate Solution. — Prepare a solution of sodium thiosulphate by dissolving five grams of the crystallized salt, $Na_2S_2O_3.5H_2O$, in one liter of water. Prepare a solution of iodine by dissolving about 2.5 grams of iodine in 100 cc. of water containing 5 grams of pure potassium iodide, and diluting, after solution is complete, to one liter. Standardize these two solutions against each other, using freshly-prepared starch solution as indicator, and then standardize the sodium thiosulphate against potassium permanganate in the following manner. Draw 10 cc. of standardized potassium permanganate solution[1] into a No. 5 beaker containing one gram of potassium iodide dissolved in 350 cc. of *cold* distilled water. Add dilute sulphuric acid by drops, until the solution has *just* cleared from precipitated manganese dioxide. The liberated iodine is then titrated with sodium thiosulphate, freshly-prepared starch paste being added when the yellow color of the iodine solution has nearly disappeared. The sharpness of the end reaction is much increased if the solution be cooled by a few lumps of ice. Knowing the value of the potassium permanganate solution, the strength of the sodium thiosulphate solution can be calculated.

METHOD

Construct an evolution apparatus as follows: Use a 250 cc. round bottom flask as a generating flask. Fit into this a doubly perforated rubber stopper, through one hole of which is passed a dropping funnel extending to near the bottom of the flask, and through the other a delivery tube bent twice at right angles. This tube leads down about an inch below the

[1] The potassium permanganate may be standardized as described on p. 21 by using sodium oxalate as standard.

rubber stopper into a 250 cc. Erlenmeyer flask. From this flask have a short tube bent at right angles and connected by rubber tubing with a second tube bent at right angles and extending to the bottom of a second Erlenmeyer flask. By a similar arrangement connect a third Erlenmeyer flask.

Place 10 cc. of a cadmium chloride solution and 50 cc. of water in the second and third absorption flasks. (Cadmium chloride solution contains 120 grams $CdCl_2$ in 1500 cc. H_2O, and 600 cc. NH_4OH, sp. gr. 0.90).

Weigh into the generating flask 5 grams of steel, and place 50 cc. of hydrochloric acid (sp. gr. 1.2) in the dropping funnel.

When the apparatus is shown by test to be tight, allow the acid to enter the flask in small portions, maintaining an even and fairly rapid flow of gas through the apparatus. When action ceases or slackens, warm gently, and finally boil the liquid until steam condenses in the empty flask. Open the stopcock of the dropping funnel, and at the same time remove the flame.

Precipitation usually takes place only in the second flask. Filter the liquid containing the cadmium sulphide precipitate. Wash out the flask twice with water containing a small amount of ammonia, then transfer the filter and precipitate to a beaker and pour over it 300 cc. of water. By means of vigorous stirring, break up the filter paper into shreds. Rinse out the guard flask and the absorption flask and tubes with 50 cc. of water to which 5 cc. hydrochloric acid (sp. gr. 1.20) has been added. This should remove all sulphide. Add this liquid to the liquid containing the filter paper and precipitate, and at once add an excess of iodine solution, titrating back with the thiosulphate solution after a few moments. Take great care to avoid loss of hydrogen sulphide before the addition of the iodine.

> *Notes.* — 1. Sulphur occurs in irons and steels in four forms: (1) iron sulphide; (2) manganese sulphide; (3) titanium sulphide; and (4) a form, or forms, not yet identified, but characterized by certain reactions. Manganese sulphide is the most commonly occurring form, and the sulphur occurs as iron

sulphide only when there is insufficient manganese present to combine with it.   The occurrence of titanium sulphide is rare, although it is occasionally found in irons made from ores carrying small amounts of titanium.   The unidentified form does not respond to the reactions of the other three forms and there is some evidence, although not by any means conclusive, that there may be a combination with carbon, or silicon, or both.

2. The effect of sulphur, when existing as iron sulphide, is to make the metal "red-short," i.e., brittle at the forging temperatures.   This effect is overcome by the addition of manganese, which converts iron sulphide into manganese sulphide.   The red-shortness is destroyed, but in some cases the sulphide of manganese is rolled out into filaments, and these, being brittle and weakly cemented to the steel surrounding them, become points of weakness.

The most important effect of sulphur is its influence upon the forms of carbon.[1]   In castings where form is more of a factor than strength, high sulphur irons may be used so as to get a very fluid metal.   In these castings the carbon is always in the combined form, and the iron is white or gray.

3. The evolution method for sulphur in steel is based upon the assumption that all of the sulphur will be evolved as hydrogen sulphide, which may be determined by titration with iodine.   The reactions involved are the following:

$$\text{I. } MnS + 2HCl = MnCl_2 + H_2S.$$
$$\text{2. } H_2S + 2I = 2HI + S.$$
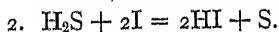
The standardization of the iodine and sodium thiosulphate solutions is based upon these reactions:

$$\text{I. } 2KMnO_4 + 10KI + 8H_2SO_4 = 6K_2SO_4 + 2MnSO_4 +$$
$$8H_2O + 5I_2.$$
$$\text{2. } 2I + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6.$$
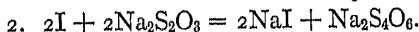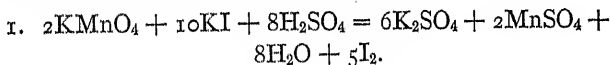
This method of standardization is most accurate and convenient if one has ready a standard potassium permanganate solution.   Other methods of standardization, such as the titration of iodine against pure arsenious acid, the titration of sodium thiosulphate against pure iodine, or the use of a steel of

[1] See note, p. 62.

known sulphur content, may be used, but the time involved is usually greater, and no greater accuracy is secured.

4. Instead of titrating hydrogen sulphide against iodine, the hydrogen sulphide may be passed directly into some oxidizing agent, such as ammoniacal hydrogen peroxide, alkaline potassium permanganate, or hydrochloric acid saturated with bromine. The sulphuric acid formed may then be precipitated and weighed as barium sulphate. Indirect oxidation may also be used by absorbing in an alkaline lead salt, or ammoniacal zinc or cadmium salts and subsequently oxidizing the sulphides formed.

5. The assumption that all of the sulphur of an iron or steel is evolved as hydrogen sulphide is not strictly correct, in fact some steels and irons yield none of their sulphur as hydrogen sulphide. Part of it may be evolved as a sulphur ether $(CH_3)_2S$, or some analogous compound, and part of it may remain as a residue unacted upon by hydrochloric acid.[1]

Phillips[2] was the first to point out that certain irons gave low results, due to loss of sulphur in combination with carbon and hydrogen. He showed that oily drops containing sulphur were formed and that sulphur in this form was not oxidized by the usual oxidizing, absorbing agents, nor did this form react with lead, zinc or cadmium salts to form sulphides. To overcome this difficulty, he proposed passing the evolved gases through a heated tube before passing into the absorbing agent. In this way the organic sulphide was broken down in the presence of hydrogen to hydrogen sulphide.

Various workers have recommended annealing the metal before placing in the evolution flask, and have obtained improved results. Elliot[3] recommends annealing in a closed muffle a five-gram sample mixed with 0.25 gram dry potassium ferrocyanide and wrapped in one 11 cm. filter paper. The best temperature for annealing is between 750° and 850° C. and the time twenty minutes. Steels so treated give satisfactory results by the evolution process.

Because of the difficulties mentioned the evolution process should never be used where an absolute value is wanted. In

[1] Blair, *J. Am. Chem. Soc.*, **19**, 114.
[2] Phillips, *J. Am. Chem. Soc.*, **17**, 891.
[3] *J. Iron and Steel Inst.*, 1911, No. 1, 412.

a majority of cases it will yield fairly accurate results, and by annealing the sample, improved results are obtained, but where there is any question of controversy the Bamber method should be employed.

6. Iodine and sodium thiosulphate solutions are subject to change, and their values should be verified frequently. The titration of iodine by sodium thiosulphate in weak acid solution gives accurate results, but the acid must be weak and the solution cool.

7. Wiborgh [1] has devised a colorimetric process for sulphur in steel, based upon the depth of color attained by a cloth treated with a cadmium salt. The evolved gases are passed through the cloth placed over the mouth of the generating vessel, and this cloth is compared either with a standard, or a steel of known sulphur content.

DETERMINATION OF SULPHUR IN CAST IRON

BAMBER METHOD [2]

Weigh five grams of borings into a 250 cc. porcelain casserole, and treat with 40 cc. of concentrated nitric acid. The reaction may be violent, and it is wise to have ready a beaker of cold water into which to dip the casserole in order to slow down the reaction. Evaporate to about one-half the volume and then add 5 grams of sodium carbonate. Transfer to a platinum dish, and evaporate to dryness, stirring the pasty mass from time to time. Ignite over an alcohol flame until the oxides of nitrogen are completely driven off. After cooling, treat with 20 cc. of a five per cent solution of sodium carbonate and bring to boiling. Allow to settle, and decant through a filter into a No. 4 beaker. Repeat this process several times. Acidulate the filtrate with hydrochloric acid, evaporate to dryness, re-dissolve in water with a few drops of hydrochloric acid, filter if necessary, and precipitate in the boiling solution with barium chloride. Allow to stand until the precipitate has settled, filter, wash, and ignite as in the analysis of pyrite.

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[1] *Stahl und Eisen*, **6**, 240.
[2] *J. Iron and Steel Inst.*, 1894, No. 1, 319.

Notes. — 1. Some steels and irons will not yield all of their sulphur in the form of sulphuric acid when treated with concentrated nitric acid or with aqua regia, nor as hydrogen sulphide on treatment with hydrochloric acid. Furthermore, the precipitation of barium sulphate in the presence of iron salts is always an uncertain and inaccurate process. In order to overcome these difficulties and to obtain all of the sulphur, a fusion process must be used. The direct fusion of the steel is a very slow and uncertain process. Bamber proposed to overcome this by a combination solution and fusion process. In this method partial oxidation is accomplished by nitric acid, and complete oxidation by fusion with sodium nitrate and by the decomposition of ferric nitrate into oxide of iron and the strongly oxidizing oxides of nitrogen. Bamber's method has the distinct advantage over other methods in that all of the sulphur, in whatever form present, is obtained, and, further, that precipitation of the barium sulphate is made in the absence of iron and under well-controlled conditions.

2. Concentrated nitric acid frequently renders steel or iron passive, and solution takes place only with difficulty. In order to hasten solution, it is advisable to add, from time to time, one or two drops of concentrated hydrochloric acid. The hydrochloric acid must never be present in excess, as loss of sulphur as sulphur dioxide will result.

3. Evaporation to dryness of the ferric nitrate solution is a tedious operation. To prevent spattering and caking of the surface, the mass must be stirred frequently.

An alcohol flame is not absolutely necessary for the ignition, but is desirable. By placing the dish in an opening in an asbestos board, gas may be used for the ignition, but the board must be large enough to deflect the products of combustion of the gas. The platinum dish is always attacked to an appreciable extent by the ignition, and the process has, therefore, the disadvantage of the wear on the platinum.

4. Sodium carbonate is used to wash out the sulphates, so as to decompose any basic salts which may be present.

5. Pulsifer[1] has recommended the use of chloric acid as solvent and oxidizing agent for the determination of sulphur in steel, and claims excellent results for the method. He says

[1] *J. Ind. Eng. Chem.*, **8**, 1115.

that the Bamber method is liable to give slightly high results on account of the tendency to absorb sulphur from outside sources, and the nitric acid oxidation method gives low results because of the solubility of barium sulphate in ferric chloride solution.

An excellent bibliography of the determination of sulphur in iron and steel is given in this paper.

DETERMINATION OF SILICON IN CAST IRON

METHOD OF DROWN

For the determination of silicon in cast iron, weigh a one-gram sample; for wrought iron and steel, weigh a three-gram sample. Treat the borings in a casserole with a mixture of 15 cc. of water and 15 cc. of nitric acid (sp. gr. 1.42). As soon as the reaction has ceased, add 25 cc. of sulphuric acid, made by mixing equal parts of the concentrated acid and water. Evaporate to dryness on the steam table and then heat over a free flame in a well ventilated hood until the sulphuric acid fumes strongly. Allow to cool and then add 150 cc. of water and 5 cc. of dilute hydrochloric acid. Heat until the solution of the ferric sulphate is complete and filter by suction *at once*. Wash with dilute hydrochloric acid (one part acid sp. gr. 1.12 to three parts of water) until the filter paper is free from iron stain, and with hot water to remove the hydrochloric acid. Place the filter and silica in a platinum crucible, char the paper slowly and ignite with the crucible on its side and the lid partially covering the mouth.

The graphite from cast iron burns off very slowly and consequently the crucible should be so placed as to have as much air as possible. When the ignition is complete, cool in a desiccator, weigh, and treat the contents of the crucible with hydrofluoric and sulphuric acids exactly as in silicate analysis. Weigh again. The difference in weight is silica.

Notes. — 1. Silicon exists in cast irons and steels for the most part in the form of a solid solution of the compound Fe_2Si in iron. In wrought iron and some low carbon steels,

part of it may also exist in the oxidized form as silicate of iron or silicate of manganese. A silicate of manganese having the composition $2MnO.3SiO_2$ has been isolated from steel by Stead.[1]

In ferro-silicon, the silicon may exist as a solid solution of the compound Fe_2Si in iron; as the compounds Fe_2Si or $FeSi$, or mixtures of these two; and as mixtures of $FeSi$ with silicon, the relative proportions of each being dependent upon the percentage of silicon present.

2. The influence of silicon in small amounts upon steel has not been well established, except in its effect upon the shrinkage in cast steels. In such steels, the excessive shrinkage can be counteracted by the introduction of silicon, the amount remaining in the metal being about 0.30 per cent. It also diminishes blow holes in castings.

In cast irons, the silicon influences the form of carbon very markedly. With increasing percentages of silicon, there is a corresponding increase in the amount of carbon in the form of graphite. While cast irons are graded upon the appearance of graphite in the fractured surface, it is the silicon which influences the character of this appearance. The appearance of the fracture is also undoubtedly influenced by temperature and time of cooling.[2]

3. Nitric acid is used in preference to hydrochloric or sulphuric acids for solution because it will decompose any titanium carbide which might be present in titaniferous pig irons. In the other acids it is insoluble and would be left in the siliceous residue.

4. Evaporation to free fuming of the sulphuric acid is necessary, otherwise there is incomplete dehydration of the silica. More complete dehydration takes place in sulphuric acid than in hydrochloric acid solutions.

Nitric acid, when being freely removed, will fume in moist air and this must not be mistaken for sulphuric acid.

During the evaporation, the ferric sulphate is liable to spatter. It is, therefore, necessary to have a watch glass of sufficient size to cover the casserole and to rotate the casserole during the final heating.

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[1] Stead, Iron and Steel Magazine, **9**, 105.
[2] Adamson, *J. I. & S. Inst.* 1911, No. 2, 86.

5. The filtration of the silica must take place soon after the solution of the ferric sulphate is complete on account of the tendency of the silica to go back into solution. Losses amounting to fully half of the total silica may occur on allowing the solution to stand over night.

6. In cast irons, the burning of the graphitic residue is a tedious operation and cannot be helped much by the use of the blast lamp. It is advisable to start this ignition, and, in the meantime, continue other work until the silica becomes white.

7. In some ferro-silicons, solution in acids takes place extremely slowly. In high silicon products such as ferro-silicon, "Duriron," etc., it is, therefore, more advantageous to fuse at once with sodium carbonate or with a mixture of sodium carbonate and sodium peroxide and to treat the fusion as in the analysis of feldspar.

DETERMINATION OF COPPER IN STEEL

Dissolve 5 grams of steel in 75 cc. of nitric acid (sp. gr. 1.20) by gently heating in a covered 250 cc. porcelain casserole. When solution is complete, add 25 cc. of dilute sulphuric acid (1 : 1) and evaporate until the acid fumes freely. Dissolve by heating with 50 cc. of water and 10 cc. of dilute sulphuric acid, filter into a 500 cc. Erlenmeyer flask and wash the silica with hot water. Dilute the filtrate to 300 cc., add 25 cc. of concentrated freshly prepared ammonium bisulphite solution, and heat to boiling. When the iron is completely reduced, add 30 cc. of a 20 per cent solution of sodium thiosulphate, and continue the boiling until the sulphide of copper is coagulated. Filter, wash with hot water, and ignite in a porcelain crucible. Dissolve in a small amount of concentrated nitric acid, nearly neutralize with ammonia, transfer to a platinum crucible and electrolyze, making the crucible the cathode. Wash the crucible with water after all of the copper is deposited, then with alcohol, dry and weigh.

Notes. — 1. Copper may be found in small amounts in nearly all steels, and is added to sheet steel in amounts, usually under 0.25 per cent, in order to retard corrosion. Steels thus

treated resist ordinary corrosive action of the weather much better than ordinary steels.

The effect of copper upon the physical properties has not been definitely determined. In high carbon steels there is a tendency for the copper not to alloy with the iron.

In high-speed tool steels copper is detrimental.

2. The principle involved in this method is dependent upon the precipitation of the copper as sulphide in a solution in which the iron has been reduced, its conversion into nitrate and the deposition of metallic copper by electrolysis.

3. Instead of depositing the copper as metal, the sulphide may be ignited and weighed as oxide, but it is always contaminated with iron and hence the results are less accurate.

The solution obtained in the evolution method for sulphur, or the filtrate from the silicon determination may be used for the precipitation of copper.

4. The purpose of the ammonium bisulphite is to reduce the iron to the ferrous condition. Sodium thiosulphate could be used, but it would involve the separation of a large amount of free sulphur.

5. The reaction between copper salts and sodium thiosulphate is complicated. The principal reaction is the reduction of the cupric ion to cuprous ion and at the same time oxidation of the S_2O_3'' ion to S_4O_6'', SO_3'' and SO_4'' ions. There are also formed complex cupro-thiosulphate ions $(CuS_2O_3)'$, which decompose in boiling solution with formation of Cu_2S.

6. The volumetric method may be used for the determination of copper. In case it is desired to do this, proceed exactly as in the Low method after having dissolved the copper sulphide in nitric acid.

DETERMINATION OF NICKEL IN STEEL

METHOD OF BRUNCK[1]

Weigh 0.5–0.6 gram of steel into a No. 4 beaker, and dissolve in 20 cc. of hydrochloric acid, sp. gr. 1.12. To the solution add about 1 cc. concentrated nitric acid and boil to oxidize all of the iron. The solution is filtered if silica has separated, or in the case of a high silicon steel, it should be

[1] *Z. angew. Chem.* (1907), 1844.

evaporated to dryness to remove silica. To the solution is added 2 to 3 grams of tartaric acid, and it is then diluted with water to about 300 cc. Add ammonia in slight excess and if no ferric hydroxide separates, make slightly acid with hydrochloric acid, and heat to near boiling. Add 20 cc. of a 1 per cent alcoholic solution of dimethylglyoxime, and ammonia, drop by drop, till present in slight excess. Allow to stand for one hour, collect the deep-red precipitate on a Gooch crucible, wash with hot water, dry at 110° for 45 minutes, and weigh as $Ni(C_4H_7N_2O_2)_2$.

Notes. — Nickel forms with iron a series of homogeneous solid solutions for all concentrations. Its addition to steel raises the strength and particularly the elastic limit without corresponding loss in ductility. (See Carbon.) By the use of nickel steel it is possible to get a greater strength with smaller cross section than with a carbon steel. For this reason it is used extensively in manufacturing parts where the total weight is an important consideration, such as in bicycle and automobile parts.

The most useful nickel steels are those which contain 2–3.75 per cent nickel, and 0.1–0.65 per cent carbon. For marine boiler tubes, condensers, etc., low carbon, 25–30 per cent nickel steels are used, which have the advantage of being more non-corrosive than carbon steels, and relatively very much lighter in weight.

Nickel affects the carbon condition to a very marked extent. Ordinary nickel steels containing 3.5 per cent of nickel, and carbon up to 0.80 per cent are pearlitic, but with increasing percentages of carbon are either martensitic or austenitic. With lower carbon these same changes are produced with increase of nickel. For example, a 0.2 per cent carbon steel is pearlitic up to 8 per cent nickel; martensitic with 12–20 per cent nickel; and austenitic above 25 per cent nickel.

2. The principle involved in the separation of nickel from iron is based upon the insolubility of nickel dimethylglyoxime[1] in slightly ammoniacal solution, the ferric oxide being held in solution in the form of a complex ion in combination with tar-

[1] Tschugæff, *Berichte*, **38**, 2520; Brunck, *Stahl und Eisen*, **28**, 331; Brunck, *Z. angew. Chem.* (1907), 1844; Prettner, *Chem. Ztg.*, **33**, 396.

taric acid. The method separates nickel from cobalt, iron, chromium, manganese, copper, tungsten, and vanadium. If much manganese is present, the separation should be made in acetic acid solution.

3. Another principle frequently used for the separation of iron from nickel is based upon the solubility in ether of ferric chloride[1] in hydrochloric acid solution, sp. gr. 1.11. By this method most of the ferric chloride can be removed not only from nickel, but from cobalt, manganese, chromium, aluminum and titanium, thus giving a simple means of removing most of the iron from these elements. This principle has also been used to advantage for the removal of iron in sulphur determinations, the ferric chloride being soluble, and the sulphate insoluble. The removal of the small amount of iron left in solution after the ether separation is a comparatively simple operation. The separation from nickel may be made by means of ammonia and ammonium chloride, or by the basic acetate process.

4. In some methods for the determination of nickel, it is necessary to remove copper first. This is so when iron is removed by means of ammonia and ammonium chloride, or by ether. The nickel is subsequently precipitated as sulphide, ignited and weighed as oxide. When nickel is determined volumetrically by means of potassium cyanide, it is also necessary to remove copper first.

DETERMINATION OF CHROMIUM IN STEEL

METHOD OF BARBA [2]

Weigh 1.5–2 grams of steel into a 300 cc. Erlenmeyer flask, and dissolve in 20 cc. sulphuric acid (1:5). If a residue remains it should be filtered off, ignited and fused with a small amount of sodium carbonate and potassium nitrate. The fusion should then be taken up in a small amount of dilute sulphuric acid and added to the main solution. Heat to boiling, and add drop by drop concentrated nitric acid until all the iron is completely oxidized. Boil off the oxides of nitrogen, dilute with boiling water to 150 cc. and add 5 cc. saturated potassium

[1] Rothe, *Mittheilungen König. Tech. Versuchs. zu Berlin*, 1892.
[2] *Iron Age*, **52**, 153.

permanganate solution or until a permanent pink color is obtained. Boil 15 to 20 minutes, and if after this time the color of the permanganate persists, add 25 cc. strong ammonia. Digest at a low heat with occasional stirring for half an hour or until the excess permanganate is destroyed. Then add cautiously 20 cc. dilute sulphuric acid (1 : 1), and heat for 1 to 2 minutes to boiling. Cool the solution to room temperature, transfer to a 250 cc. graduated flask and dilute to the mark. Mix thoroughly by pouring back and forth into a dry beaker. Allow the precipitate to settle, filter through a 4-inch Swedish filter, rejecting the first few cc.; measure off 200 cc. of the clear filtrate, add an excess of standard ferrous sulphate, and determine the excess by means of standard potassium permanganate.

Notes. — 1. Chromium as a constituent of steel has the effect of increasing the strength and the hardness, and chrome steels are always finer grained than plain carbon steels. They are always used in the heat treated condition and the properties are susceptible of great modifications by heat treatment. Where extreme hardness is desirable, chrome steels are used and for dies, rolls for cold rolling metals, balls, and roller bearings give excellent service. The Ac_1 point is slightly raised, and, therefore, chrome steels must be hardened at a higher temperature than plain carbon steels.

Chrome-nickel steels have many desirable properties in the heat-treated condition and are used extensively, particularly in automobile parts. For such uses the chromium may vary from 0.50 per cent to 1.50 per cent and the nickel from 1.25 per cent to 3.50 per cent.

These steels are also used for armor plate and projectiles.

Mayari steel is made from an ore mined in Mayari, Cuba, which contains chromium and nickel. This steel is used for rails and automobile parts.

High speed tool steels contain chromium and tungsten with about 2.50 to 5.00 per cent of chromium and about 18.00 per cent of tungsten. They may be free from vanadium, but most of those on the market now carry small amounts (0.50–2.00 per cent) of this element.

2. The principles involved in this method are based on the oxidation of chromium to chromic acid in dilute sulphuric acid solution by means of concentrated potassium permanganate, the reduction of the chromic acid by means of ferrous sulphate, and the estimation of the excess ferrous sulphate by means of standard potassium permanganate solution. The reactions involved in the calculation of results are as follows:

1. $H_2Cr_2O_7 + 6FeSO_4 + 6H_2SO_4 = 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + 7H_2O.$

2. $2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$
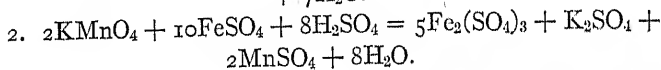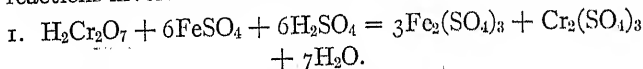
3. Chromium and iron may be separated by means of ether in the same manner as nickel and iron. The solution containing the chromium ions may be oxidized to chromate ion, and then determined either by gravimetric or volumetric means.

4. The iron is oxidized with nitric acid in order to avoid the use of a larger amount of potassium permanganate and the subsequent formation of large quantities of manganese salts and of manganese dioxide.

5. The value of the ferrous sulphate solution in terms of potassium permanganate should be determined each day before using.

6. Sodium bismuthate may be used to oxidize chromium from the trivalent to the hexavalent condition if added to the *hot* solution. The chromic acid formed is not decomposed in the boiling solution, and it may be separated by filtration from excess sodium bismuthate and from precipitated manganese dioxide.

DETERMINATION OF CHROMIUM IN CHROME-VANADIUM STEEL

METHOD OF CAIN [1]

Weigh 1–2 grams of steel into a 300-cc. Erlenmeyer flask, and dissolve in concentrated hydrochloric acid, using 10 cc. of acid per gram. When solution is complete dilute to 150 cc. with hot water, and add saturated sodium carbonate solution until nearly neutralized. Add barium carbonate emulsion in

[1] *J. Ind. Eng. Chem.,* **4,** 17.

slight excess, boil vigorously 10–15 minutes, with small additions of emulsion every two or three minutes. Not more than 1–2 grams excess of barium carbonate should be added, and care should be exercised to keep the flask covered as much as possible while adding it.

Remove the flask from the heat, allow the precipitate to settle and filter on an 11 cm. filter paper, washing twice with hot water. Ignite the precipitate in a platinum crucible, mix with two grams of sodium carbonate and 0.25 gram potassium nitrate. Fuse for 20 minutes.

Extract the melt by placing the crucible on the bottom of a small beaker and covering with hot water. Filter into an Erlenmeyer flask, add 1 or 2 cc. of hydrogen peroxide and boil for five minutes to destroy the excess. Add a slight excess of nitric acid, shake vigorously to remove carbon dioxide. Transfer to a 250 cc. beaker, and add 2 cc. dilute (1 : 1) nitric acid for each 100 cc. of solution. Add 20 cc. of a 20-per cent solution of lead nitrate with constant stirring. Filter on asbestos, wash several times with cold water. Transfer the asbestos mat to a beaker and decompose the lead chromate with hot dilute (1 : 4) hydrochloric acid. Cool the solution, dilute to 200 cc. and titrate with standard ferrous sulphate solution, using potassium ferricyanide as outside indicator.

Notes. — 1. The principle of this method is based upon the precipitation in boiling solution of chromium hydroxide, in presence of ferrous iron, and the subsequent oxidation of chromium to chromate, the latter being measured by a standard ferrous sulphate solution.

2. Noyes and Bray[1] have studied the conditions for the separation of chromium and vanadium, and find that by boiling with barium carbonate all of the chromium is precipitated, and the separation from vanadium is complete. To further insure separation Cain separates chromium as lead chromate under conditions which would prevent vanadium being precipitated.

3. The addition of hydrogen peroxide is for the removal of

[1] *Tech. Quart.* (1908), **21**, 14.

any nitrite which if present might, on acidifying, reduce chromium or vanadium. The excess hydrogen peroxide must be removed as it would reduce chromic acid.

4. The removal of carbon dioxide is simply for the purpose of getting a precipitate which will settle rapidly.

DETERMINATION OF TUNGSTEN IN STEEL

Weigh 2-5 grams of sample into a porcelain casserole and dissolve in 60 cc. nitric acid (sp. gr. 1.20) with the addition, from time to time, of a few drops of strong hydrochloric acid. If the precipitated tungstic acid is dark colored, digest for some time with occasional addition of a few drops of hydrochloric acid until the precipitate becomes a light yellow.

Evaporate the solution to dryness and heat to decompose nitrates. Moisten with concentrated hydrochloric acid and evaporate to dryness. Take up in concentrated hydrochloric acid and warm until all ferric oxide is in solution. Evaporate off the excess of hydrochloric acid, and continue until the solution becomes syrupy. Dilute with 50-75 cc. of dilute hydrochloric acid, stir, allow to settle and filter. Wash the precipitate on to the filter with dilute hydrochloric acid (1 : 5), adding some paper pulp if there is any tendency to pass through the filter paper; and complete the washing with hydrochloric acid. Remove any tungstic oxide adhering to the casserole with a small piece of filter paper moistened with ammonia, add to the precipitate, ignite over a Tirrill burner, at first at a low temperature, and finally at full heat.

Treat with 2-3 drops of sulphuric acid and about 2-3 cc. of hydrofluoric acid, evaporate to remove silica, and ignite.

Fuse with six times its weight of sodium carbonate, allow to cool, digest with hot water, and filter, washing the residue with hot water. Nearly neutralize the filtrate with nitric acid, boil off carbonic acid, allow to cool, and make *slightly* acid with nitric acid. Add mercurous nitrate[1] solution to the gently boiling solution, allow to settle and test with more

[1] 100 grams of salt dissolved in one liter of water, to which some free mercury has been added.

mercurous nitrate. Then add an emulsion of mercuric oxide and water until excess nitric acid is neutralized. Allow the precipitate to settle, filter, wash several times by decantation, adding a few drops of mercurous nitrate solution to the hot water, and finally wash with water.

Dry and ignite the precipitate in a porcelain crucible and weigh as WO_3.

Notes. — 1. Steels containing about 6 per cent of tungsten and about 0.60 per cent of carbon are extensively used in the hardened condition for permanent magnets. When used for electric meters they are seasoned, after hardening, by heating for a long time at 100°. Tools for making finishing cuts at relatively high speed are made of steels containing 1 per cent of carbon and 3–4 per cent of tungsten. According to Arnold and Read [1] carbon is combined with iron in low tungsten steels, but with increasing tungsten more of the carbon enters into combination with it and in steels containing 11.5 per cent or more all of the carbon is in combination with tungsten.

High speed steels contain 13–18 per cent of tungsten, 2.5–5.00 per cent of chromium, 0.60–0.70 per cent of carbon, and usually under 1.00 per cent of vanadium. They are characterized by their ability to be worked at a speed 3–5 times greater than with plain carbon steels, and to maintain their hardness at a red heat ("red-hardness"). These steels are hardened at a temperature, white heat, which would ruin a plain carbon steel. It is believed that at the high temperature which is necessary for satisfactory hardening, double carbides [2] of chromium and tungsten are formed, which persist on rapid cooling, and also to some extent on slow cooling.

2. The principle of this method is dependent upon the precipitation of tungstic acid anhydride, WO_3, from an oxidizing acid solution. This precipitate is subsequently converted into mercurous tungstate, ignited and weighed as WO_3.

3. If the residue obtained after removal of silica is weighed, it will give a fairly accurate result for tungsten. This residue, however, invariably contains traces of iron, chromium, and manganese, and it is the purpose of the fusion with sodium

[1] *Proc. Inst. Mech. Eng.* (1914), 223.

[2] Edwards, *J. I. and S. Inst.*, 1908, **2**, 104.

carbonate to remove tungsten as soluble sodium tungstate from the elements.

4. In ferro-tungsten and tungsten metal, insoluble in acid, decomposition may be accomplished by fusing the powdered metal with a mixture of sodium carbonate and potassium nitrate, or with Eschka[1] mixture. In either case the product is soluble sodium tungstate which may be precipitated as mercurous tungstate and ignited to tungstic acid.

DETERMINATION OF VANADIUM IN STEEL

Dissolve a 2-gram sample in 20 cc. of hydrochloric acid (sp. gr. 1.20) adding sufficient nitric acid to completely oxidize the iron. Evaporate to small volume, and in case tungstic acid separates, dilute, filter, wash with dilute hydrochloric acid, and evaporate the filtrate to a syrupy consistency. Pour the solution into a separatory funnel, and wash the casserole free from ferric chloride by successive small additions of hydrochloric acid (sp. gr. 1.10), taking care to keep the volume small. Add an equal volume of ether, and shake for several minutes, releasing the pressure occasionally by opening the stopcock of the funnel, holding the tube of the funnel pointing upward and allowing time for any ejected solution to return into the bulb. Draw off the hydrochloric acid solution from the ether layer into a second separatory funnel and repeat the shaking with ether.

Again separate the hydrochloric acid layer from the ether, and evaporate to small volume. Convert the hydrochloric acid solution into a nitric acid solution by several evaporations to small volume after the addition of some concentrated nitric acid between evaporations. Dilute slightly with water, add two or three drops of sulphurous acid, heat to boiling and pour *slowly* into 100 cc. of boiling sodium hydroxide solution (100 grams per liter). Boil a few minutes, filter, and wash with hot water. Acidify the filtrate slightly with nitric acid, make slightly alkaline with sodium hydroxide and boil.

[1] See page 48.

Filter, and to the filtrate add 10 cc. of a solution of lead acetate, and then enough acetic acid to give a decided odor. Heat to boiling and filter off the lead vanadate on asbestos, washing with hot water. Dissolve by pouring through the precipitate hot dilute hydrochloric acid. Evaporate nearly to dryness, add 50 cc. concentrated hydrochloric acid and again evaporate. Add 10 cc. concentrated sulphuric acid and evaporate until the acid fumes freely. Cool, dilute to 150 cc. and titrate with dilute potassium permanganate, keeping the solution at a temperature of 60–70°.

Notes. — 1. The so-called vanadium steels nearly always contain chromium and should in reality be called chrome-vanadium steels. Many plain carbon steels have been treated with vanadium, and some of them contain the element in small amounts, the treated metal having desirable properties. The amount of vanadium contained in them is so small that there is no more reason why they should be called vanadium steels than the ordinary steel should be called manganese steel on account of its having been treated with ferro-manganese. These steels probably have greater fatigue resisting qualities than plain carbon steels.

Chrome-vanadium steels are extensively used in the manufacture of automobiles and are used in those parts where it is desirable to have high elastic limit and at the same time high ductility. Such steels contain approximately 1.00 per cent of chromium and 0.20 per cent of vanadium, the carbon content varying, depending upon the use.

Vanadium is frequently used in high-speed tool steels in amounts varying from 0.40 to 2.50 per cent, but is usually under 1.00 per cent. The steels containing vanadium are supposed to have superior properties.

2. Advantage is taken of the solubility of ferric chloride in ether to separate most of the iron from vanadium. The remainder of the iron, chromium, manganese, nickel, and copper are separated by means of sodium hydroxide. The vanadium is then separated as lead vanadate, subsequently being reduced by hydrochloric acid to vanadyl salt and then oxidized in sulphuric acid solution with potassium permanganate to vanadic acid.

The essential reactions involved are the following:

$$Pb_3(VO_4)_2 + 6HCl = 3PbCl_2 + 2H_3VO_4,$$
$$2H_3VO_4 + 6HCl = 2VOCl_2 + 6H_2O + Cl_2,$$
$$VOCl_2 + 2H_2SO_4 = VOSO_4 + 2::Cl,$$
$$10VOSO_4 + 2KMnO_4 + 8H_2SO_4 = 5V_2O_2(SO_4)_3 + K_2SO_4$$
$$+ 2MnSO_4 + 8H_2O.$$
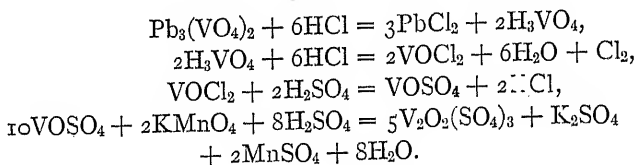
3. The Rothe[1] separation of ferric chloride by means of ether is an extremely useful process and may be applied to the separation of iron from chromium, aluminum, titanium, nickel, and manganese. When these elements are present in relatively small amounts, it serves as a convenient process for concentrating them from the larger amount of iron.

Molybdenum chloride[2] is also soluble in ether and in a separation will be found with the ferric chloride, from which it may be separated as sulphide by precipitating under pressure with hydrogen sulphide. It may then be converted into sulphate, reduced as in the method for phosphorus, and titrated with potassium permanganate.

4. It is necessary to convert the hydrochloric acid solution into nitric acid solution on account of using lead acetate as a precipitant. The removal of one volatile acid by another is not a question of the strength of the acid removed, but one of volatility and the amount of acid which is present in excess.

Precautions must be used in evaporating nitric acid solutions containing large amounts of iron as hydrolyzed products separate which are soluble only in hydrochloric acid.

5. The few drops of sulphur dioxide are to reduce any chromium which may have been oxidized to chromate ions, and the second treatment with sodium hydroxide removes all of the chromium and nickel.

6. Some difference of opinion has been expressed as to the reduction of vanadium by means of hydrochloric acid. Campagne[3] has obtained satisfactory results, and others have verified his results. Apparently the conditions must always be the same, and in order to avoid variations some workers prefer reduction with sulphurous acid.

[1] Rothe, *Mittheilungen König. Tech. Versuchs. zu Berlin,* 1892.

[2] Blair, *J. Am. Chem. Soc.,* **30,** 1228.

[3] *Comptes Rendus* (1903), **137,** 570.

INTERNATIONAL ATOMIC WEIGHTS, 1917.

	Symbol.	Atomic Weight		Symbol.	Atomic Weight.
Aluminum.........	Al	27.1	Neodymium.........	Nd	144.3
Antimony	Sb	120.2	Neon...............	Ne	20.2
Argon.............	A	39.88	Nickel..............	Ni	58.68
Arsenic............	As	74.96	Niton (radium emana-		
Barium............	Ba	137.37	tion)...............	Nt	222.4
Bismuth...........	Bi	208.0	Nitrogen............	N	14.01
Boron.............	B	11.0	Osmium.............	Os	190.9
Bromine...........	Br	79.92	Oxygen.............	O	16.00
Cadmium..........	Cd	112.40	Palladium...........	Pd	106.7
Caesium...........	Cs	132.81	Phosphorus..........	P	31.04
Calcium...........	Ca	40.07	Platinum............	Pt	195.2
Carbon............	C	12.005	Potassium...........	K	39.10
Cerium............	Ce	140.25	Praseodymium.......	Pr	140.9
Chlorine...........	Cl	35.46	Radium.............	Ra	226.0
Chromium.........	Cr	52.0	Rhodium............	Rh	102.9
Cobalt.............	Co	58.97	Rubidium...........	Rb	85.45
Columbium........	Cb	93.1	Ruthenium..........	Ru	101.7
Copper............	Cu	63.57	Samarium..........	Sa	150.4
Dysprosium.......	Dy	162.5	Scandium...........	Sc	44.1
Erbium...........	Er	167.7	Selenium...........	Se	79.2
Europium.........	Eu	152.0	Silicon.............	Si	28.3
Fluorine..........	F	19.0	Silver...............	Ag	107.88
Gadolinium.......	Gd	157.3	Sodium.............	Na	23.00
Gallium..........	Ga	69.9	Strontium..........	Sr	87.63
Germanium.......	Ge	72.5	Sulphur............	S	32.06
Glucinum.........	Gl	9.1	Tantalum...........	Ta	181.5
Gold.............	Au	197.2	Tellurium...........	Te	127.5
Helium...........	He	4.00	Terbium............	Tb	159.2
Holmium..........	Ho	163.5	Thallium...........	Tl	204.0
Hydrogen.........	H	1.008	Thorium............	Th	232.4
Indium...........	In	114.8	Thulium............	Tm	168.5
Iodine............	I	126.92	Tin......	Sn	118.7
Iridium...........	Ir	193.1	Titanium............	Ti	48.1
Iron,.............	Fe	55.84	Tungsten............	W	184.0
Krypton...........	Kr	82.92	Uranium............	U	238.2
Lanthanum........	La	139.0	Vanadium...........	V	51.0
Lead.............	Pb	207.20	Xenon..............	Xe	130.2
Lithium...........	Li	6.94	Ytterbium (Neoytter-		
Lutecium..........	Lu	175.0	bium)..............	Yb	173.5
Magnesium........	Mg	24.32	Yttrium.............	Yt	88.7
Manganese........	Mn	54.93	Zinc................	Zn	65.37
Mercury...........	Hg	200.6	Zirconium...........	Zr	90.6
Molybdenum	Mo	96.0			

LOGARITHMS OF NUMBERS

Natural numbers.	0	1	2	3	4	5	6	7	8	9	Proportional Parts								
											1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

LOGARITHMS OF NUMBERS (*Continued*)

Natural numbers.	0	1	2	3	4	5	6	7	8	9	PROPORTIONAL PARTS.								
											1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9026	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9666	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	978	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

ANTILOGARITHMS

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.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	2	2	2	2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
.37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
.38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
.48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
.49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6

ANTILOGARITHMS (*Continued*)

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.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
.52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
.53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
.55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
.56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
.57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
.58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
.59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
.61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
.62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
.63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
.64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
.65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
.66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
.67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
.68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
.69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
.70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
.71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
.72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
.73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
.74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
.75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
.76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
.77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
.78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
.79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
.80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
.81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
.82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
.83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
.84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
.85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
.86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
.87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
.88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
.89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
.90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
.91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
.92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
.93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
.94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
.95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
.96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
.97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
.98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
.99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20

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